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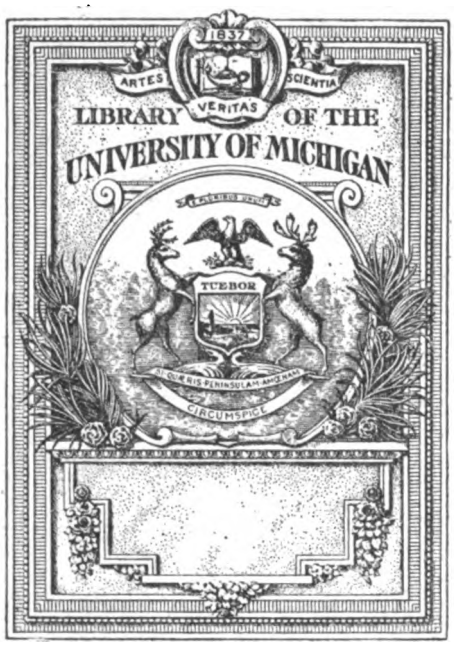

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CONTENTS

Forward - - - - - - - - - 1
Report on Tannin. By William H. Krug - - - - 2
Amended and Adopted Report of the Committee on Recommendations in Relation to Methods for Analysis of Tanning Materials - - 12
Report on Tannins. By John H. Yocum, Associate Referee - 13
Preparation of Tanning Extracts for Analysis. By Robert H. Forbes 21
Report on Tannins. By J. H. Yocum, Referee - - - 25
Report on Tannin. By Oma Carr, Referee - - - 41
A Comparison of the International Filter-Tube Method and the Official Hide Powder Method. By H. W. Wiley and William H. Krug 51
Report on Tannin. By W. K. Alsop, Referee - - - 54
Report on Meeting of the International Association of Leather Trades Chemists, 1901. By W. H. Krug - - - - 75
Report on Tannin. By W. H. Teas, Referee - - - 78
Report on Tannin. By G. A. Kerr, Referee - - - 87
Report on Tannin. By G. A. Kerr, Referee - - - 95
The Extraction of Tanning Materials With Different Extractors. By F. P. Veitch - - - - - - - - 119
A Discussion of Methods for the Estimation of Tannin. By F. P. Veitch 122

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American Leather Chemists Association

INDEX TO VOLUME XV, 1920

Numbers refer to pages. (A) indicates an abstract. (P) a patent.
Patents relating to leather working machinery are not indexed.

INDEX TO AUTHORS' NAMES

ALSOP, W. K., Report on Tannin 54
ANTHES, J. F. (see Terrasse, G. L.).
ATKIN, W. R. (see Thompson, F. C.).
ATKIN, W. R., AND W. E. PALMER, The Analysis of Lime Liquors. Committee on Limeyard Control, II 620

BALDRACCO, G., AND S. CAMILLA, The Shake Method and Filter Method in the Analysis of Tanning Materials with Hide Powder 201
BALDRACCO, G., AND S. CAMILLA, The Preparation of Lightly Chromed Hide Powder for Analysis. (A) 544
BALDRACCO, G., AND S. CAMILLA, A Modified Shake Method for the Analysis of Tanning Materials. (A) 545
BALDWIN, M. E. (see Thomas, A. W.).
BENNETT, H. G., Lyotrope Influence and Adsorption in the Theory of Wet Work. (A) 437
BERG, A., Hide Stretcher. (P) 550
BERNARD, C., Leather Making. (P) 648
BLACKADDER, T. (see Schultz, G. W.).
BLACKADDER, T., AND C. L. GARLAND, Need of a Standard Method for Color Determination 181
BLATZ, W. C., Manufacture of Leather. (P) 337
BLATZ, F. J., Process of Dampening Leather. (P) 648
BLOCKEY, J. R., Chromium Salts. Tanning. (P) 217
BLOCKEY, J. R., Some Unsolved Problems in Leather Making. (A) .. 444
BLOXAM, A. G., Synthetic Tanning Agents. (P) 447
BOGUE, R. H., Properties and Constitution of Glues and Gelatines. (A) 632
BOURION, F., AND A. SENECHAL, On the Evolution and Oxidation of Chromic Hydroxide in Alkaline Solution. (A) 331
BOWKER, R. C., AND J. B. CHURCHILL, Effects of Oils, Greases and Degree of Tannage on the Physical Properties of Russet Harness Leather. (A) 600
BRACEWELL, R. S., The Molecular Mechanism of Colloidal Behavior. (A) 212
BROWN, J. M., Tanning Process. (P) 218
BROWNE, F. L., The Proximate Analysis of Commercial Casein. (A) .. 213
BRUN, HANS, Process of the Production of Tanning Extracts from Waste Sulphite Lye. (P) 336
BUCKOW, W., Corinal, a New Synthetic Tan-Stuff. (A) 603
BUMCKE, C. G., Neutralization of Sulphonated Oils with Ammonia, Soda and Potash. (A) 672
BURTON, D., Committee on Limeyard Control. I. The Analysis of Lime Liquors 308
BURTON, D., Chrome Tanning I. (A) 673

CALDWELL, A. R., Dressing for Leather and Leather Substitutes and Process of Making the Same. (P) 448

379670

Digitized by Google

CAMILLA, S. (see Baldracco, G.).
CARR, OMA, Report on Tannin..... 41
CASABURI, V., Notes upon Tanning with Iron Salts. (A)..... 176
CHRISTENSON, G., Composition of Matter for Use as a Substitute for Leather and Similar Purposes. (P)..... 337
CHURCHILL, J. B. (see Bowker, R. C.).
CLAFLIN, A. A., The Measurement of the Plumping Power of Solutions 234
CLARK, W., Tanning. (P)..... 338
COOMBS, F. A. (see McGlynn, W.).
CORMACK, H. M., Drying Chestnut Extract by the Cardem Process. (A) 500

DAS, S. R. (see Dhavale, B. B.).
DEAN, E. W., AND D. D. STARK, A Convenient Method for the Determination of Water in Petroleum and Other Emulsions. (A)... 435
DHAVALE, B. B., AND S. R. DAS, Effect of Neutral Salts on the Basicity of Chrome Liquors. (A)..... 673
DOERFLINGER, W. F., Pyroxylin Composition and Process of Making Same. (P)..... 218
DRURY, W., Leather Compositions. (P)..... 338
DURIO, E., Making Leather. (P)..... 447

EGLENE, L., Science Applied to the Leather Industry. (A)..... 176

FAHRION, W., On the Retention of Fat in Leather. (A)..... 334
FAHRION, W., Theory of Leather Formation. (A)..... 677
FALLOT, B., Agricultural Utilization of Tanning Wastes. (A)..... 534
FARRAR, J. H., Leather Making. (P)..... 648
FLANAGAN, J. U., Machine for Seasoning or Finishing Leather. (P).. 648
FORBES, R. H., Preparation of Tanning Extracts for Analysis..... 13
FORSE, L., Manufacture of Mocha Leather. (P)..... 550
FOSTER, S. B. (see Thomas, A. W.).
FREY, R. W., Epsom Salts in Leather, 1920 Committee Report..... 406

GALLUN, E. A. (see Wilson, J. A.).
GARLAND, C. L. (see Blackadder, T.).
GAYLEY, C. T., The Extraction of Chestnut Wood..... 344
GERNGROSS, O., Coloration of Animal Hides by Means of O-Vanillin and O-Protocatechuic Aldehyde and Tanning with Aldehyde. (A) 534
GERNGROSS, O., Formol Titration of Hide Powder and Aldehyde Tannage. (A)..... 677
GILARDINI, F., Tanning Leather for Belts. (P)..... 218
GIUSIANA, H., Practical Method for the Extraction of Tanning Material in the Tannery. (A)..... 499
GIUSIANA, H., Recovering Chrome Salts from Old One-Bath Chrome Liquors. (A)..... 499
GRASSER, G., Chemical Control of Iron Tanning. (A)..... 630
GRASSER, G., Contribution to the Study of Unhaired Skins. (Determination of Lime in Unhaired Skins.) (A)..... 675
GRASSER, G., The Speed Rate of Deliming. (A)..... 679
GREENWOOD, C. V., Tanning. (P)..... 648
GRIFFITH, R. W., President's Address to the Seventeenth Annual Meeting..... 341
GRILICHES, E., Single-Bath Chrome Tanning. (A)..... 631
GUILLIN, R., Study of Nitrification of Leather and Oil Cake. (A)... 534

HARRISON, A. P. (see Scales, F. M.).
HARRIS, W. O., Dressing for Leather and Painted and Varnished Surfaces. (P)..... 337

Digitized by Google

HART, R., The Determination of Inorganic Impurities in Sulphated Oils 404
HART, R., The Determination of Total Saponifiable Matter in Sulphated Oils by Difference 495
HARVEY, A., Sugars in Mimosa Bark and Extracts. (A)..... 245
HARVEY, A., Utilization of Leather Wastes. (A)..... 631
HAWKINS, A. J., Process of Treating Leather. (P)..... 336
HENNING, S. B., Glue and Process for Making Same. (P)..... 337
HEYL, C., Enamelled or Patent Leather. (P)..... 447
HINTZ, E., AND H. SCHULZ, Method of Drying Patent Leather. (P).. 647
HIRTH, C. A., Machine for Skiving Leather. (P)..... 647
HOLLANDER, C. S., Unhairing of Hides and Skins by Enzyme Action.. 477
HOMMON, H. B., The Purification of Tannery Wastes. (A)..... 441
HOU, TE-PANG, On the Volumetric Determination of Chromium in Chrome Leather 367
HOUBEN, LOUIS, Chrome Tanning. (A)..... 252
HOUBEN, LOUIS, Modern Sole Leather Tanning. (A)..... 644
HOUGH, A. T., Tanning with Silica. (A)..... 174
HOUGH, A. T., Determination of Bisulphites in Extracts. (A)..... 644
HOUGH, A. T., Nature of the Insolubles in Tanning Extracts. (A)... 645
HURTY, J. N., Hemlock Reds..... 15a

JALADE, M., The Analysis of Sole Leather; the Determination of Water Soluble Matter by the French and English Method. (A)..... 247
JALADE, E., Determination of the Permeability to Water of Sole Leather. (A) 537, 645
JALADE, E., Magnesium Sulphate in Vegetable Tanned Leather and Its Effect upon Analytic Results. (A)..... 674
JEDLICKA, J., Tannin Analysis. (A)..... 216
JETTMAR, J., Use of Formaldehyde in Leather Manufacture. (A).... 644

KELLEMS, T. O. (see Patten, H. E.).
KELLY, M. W. (see Thomas, A. W.).
KERN, E. J. (see Wilson, J. A.).
KERN, E. J., The Determination of Sulphate in Sulphonated Oils. (A) 535
KERR, G. A., Report on Tannin.....87, 95
KOETZLE, A., Synthetic Tanning Agents. (P)..... 549
KOETZLE, A., Tanning Material and Method of Producing Same. (P) 550, 646
KOHNSTEIN, B., Formaldehyde in the Tannery. (A)..... 436
KOHNSTEIN, B., Use of Sodium Sulphite and Sodium Bisulphite in the Tannery. (A) 674
KOHL, F., Leather Dyeing. (A)..... 444
KNOWLES, G. F., Note on the Detection of Sulphite Cellulose in Tanning Extracts. (A) 245
KROUSE, C., Art of Tanning. (P)..... 549
KROUSE, C., Degreasing Apparatus. (P)..... 550
KRUG, W. H., Report on Tannin.....1a, 2
KRUG, W. H., Report on Meeting of the International Association of Leather Trades Chemists 1901..... 75

LAMB, M. C., Detanning Chrome Leather, Glue, etc. (P)..... 218
LANSDOWN, S. C., Utilizing Scrap Leather. (P)..... 337
LAUFFMANN, R., Progress in Tanning in the Year 1918. (A)..... 254
LAUFFMANN, R., Simplified Method for the Determination of the Molybdenum Value. (A) 435
LAUFFMANN, R., Notes on the Work of Baldracco and Camilla on the Shake and Filter Method. (A)..... 645
LAUFFMANN, R., Tanning Chemistry and Technique in 1919. (A).... 680

Digitized by Google

LEVI, L. E., Complete Analysis of Chrome Leather, 1920 Committee Report 269
LEVIN, B., Tanning Compound. (P)..... 218
LLOYD, D. J., On the Swelling of Gelatine in Hydrochloric Acid and Caustic Soda. (A) 640
LOOSE, J., Leather Paring Machine. (P)..... 647
LYNAH, J., Process of Producing Artificial Leather and Product Thereof. (P) 648

MATOS, L. J., Some Considerations on the Testing of Dyes for the Leather Industry 553
MATTHAEI, J. W., Composition of Matter for Use as a Leather Substitute. (P) 336
MELAMID, M., Synthetic Tanning Agents. (P)..... 338
MERCIER, D., Machine for Treating Hides and Skins. (P)..... 647
MCGLYNN, W., F. A. COOMBS, ET AL., Tannins from Wattle Bark. (A) 604
MCLAUGHLIN, G. D., The Swelling of Limed and Hydrated Hide in the Presence of Acid or Alkali..... 228
MCLAUGHLIN, G. D., AND R. E. PORTER, On the Swelling and Falling of White Hide in Vegetable Tan Liquors..... 557
MILLER, G., Artificial Leather. (P)..... 549
MOELLER, W., Theory of the Process in the Oiling of Leather. (A).. 176
MOELLER, W., Oil Tannage. (A).....214, 676
MOELLER, W., Hydrocarbon Tannage. (A)..... 214
MOELLER, W., The Tannins of the Acacia. (A)..... 215
MOELLER, W., The Nature of Quebracho Tannin. (A)..... 678

NIHOUL, E., Synthetic Tannins and Their Use in the Tannery..... 156

PARSON, F. R., Leather in the British Engineering Trades. (A)..... 245
PARSON, F. R., Uses for Waste Ends of Leather Belting. (A)..... 629
PATTEN, H. E., AND T. O. KELLEMS, Acidity of Ash-Free and Commercial Gelatine Solutions. (A)..... 632
PECK, C. L., Recovery of Proteids from Waste Liquors of the Hide-Treating Art. (P) 647
PERICAUD, H., The Treatment of the Warble. (A)..... 433
PERICAUD, H., A Critical Study of the Warble in Reply to the Incorrect Statements of C. Vaney. (A)..... 544
PICKERING, G. F., The Commercial Examination of Sulphonated Oils. (A) 630
PICKLES, J. E., Estimation of Sulphide, Committee on Limeyard Control, III. (A) 673
PORTER, R. E. (see McLaughlin, G. D.).
POTO, M., Staining of Leather or Skins. (P)..... 646
PRINCE, J. D., Leather Substitute. (P)..... 448
PROCTER, H. R., Note on the Swelling of Gelatine in Hydrochloric Acid and Caustic Soda. (A)..... 642

REUBIG, C. R., AND O. M. SEEMANN, Leather. (P)..... 337
ROBINSON, R. H., The Determination of Formaldehyde in Solution. (A) 535
ROCIC, I., Barking Machine. (P)..... 337
ROGERS, ALLEN, Industrial Uses for the Shark and Porpoise..... 241
ROGERS, ALLEN, Process of Making Leather. (P)..... 647
ROGERS, J. S., Determination of Glucose in Leather, 1920 Committee Report 411
RÖHM, O., Treating Leather. (P)..... 217

Digitized by Google

SELTZER, J. M., Definition of Total Ash in Leather..... 130
SELTZER, J. M., Total, Soluble and Insoluble Ash in Leather, 1920 Committee Report 270
SENECHAL, A. (see Bourion, F.).
SEYMOUR-JONES, A., Leather Working and Like Machines. (P)..... 217
SCALES, F. M., AND A. P. HARRISON, Boric Acid Modification of the Kjeldahl Method for Crop and Soil Analysis. (A)..... 330
SCHELL, E., A Criticism of Baldracco and Camilla's Modification of the Official Method. (A)..... 546
SCHELL, E., What Do We Really Determine as Vegetable Tanning Matter? 669
SCHIAPARELLI, C., Vegetable Tanning: Chemical and Theoretical Considerations. (A) 253
SCHLINK, F. J., Leather Measuring Machines. (A)..... 599
SCHORLEMMER, K., New Filters. (A)..... 600
SCHULTZ, G. W., The Analysis of Sulphonated Oils, 1920 Committee Report 283
SCHULTZ, G. W., AND T. BLACKADDER, Some Observations on the Determination of the True Tanning Value of Extracts According to Wilson and Kern 654
SCHULZ, H., Method of Treating Varnished (Patent) Leather. (P).. 218
SMAIC AND WLADIKA, Leather Greases in the Years 1914-1918. (A).. 676
SMALL, F. H., The Sampling and Preparation of Sole and Harness Leather for Analysis. Preliminary Committee Report..... 475
SOMERVILLE, A. A., Artificial Leather. (P)..... 448
SPEED, BUCKNER, Invention, Research, Engineering, Manufacture..... 516
SPENCER, J. E., Leather Graining, Boarding or Softening Machine. (P) 337
STARK, D. D. (see Dean, E. W.).
STIASNY, E., Nature of the Liming Process. (A)..... 172

TAMBACH, R., Process for Producing Tannate-Lime Compound Difficultly Soluble in Dilute Acids. (P)..... 648
TEAS, W. H., Report on Tannin..... 78
TERRASSE, G. L., AND J. F. ANTHES, The Determination of Water Soluble in Leather. 1920 Committee Report..... 581
TERRASSE, G. L., Hide Substance..... 608
TERRY, G. O., Leather Skiving Machine. (P)..... 447
THOMAS, A. W., Tabulation of Hydrogen and Hydroxyl Ion Concentrations of Some Acids and Bases..... 133
THOMAS, A. W., Emulsions—Theory and Practice..... 186
THOMAS, A. W., Estimation of the Tryptic Activity of Bating Materials 221
THOMAS, A. W., The Determination of Sulphuric Acid in Leather.... 504
THOMAS, A. W., Order of Diffusion of Tanning Extracts through Gelatine Jelly and Their Relation to Results Obtained by Wilson and Kern 593
THOMAS, A. W., M. E. BALDWIN AND M. W. KELLY, Time Factor in the Adsorption of the Constituents of Chrome Liquor by Hide Substance 147
THOMAS, A. W., AND M. E. BALDWIN, Contrasting Effects of Chlorides and Sulphates on the Hydrogen Ion Concentrations of Acid Solutions. (A) 330
THOMAS, A. W., AND M. W. KELLY, The Time Factor in the Adsorption of Chromic Sulphate by Hide Substance..... 487
THOMAS, A. W., AND M. W. KELLY, Rapid Estimation of Chromium in Chrome Liquor by Use of the Immersion Refractometer..... 665
THOMAS, A. W., AND S. B. FOSTER, Titration of Chrome Liquors by the Conductance Method 510
THOMPSON, F. C., Structure of Gelatine Solutions. (A)..... 244

Digitized by Google

THOMPSON, F. C., Leather and Glue..... 380
THOMPSON, F. C., AND W. R. ATKIN, Note on the Analysis of Lime Liquor. (A)..... 245
THUAU, U. J., The New Nance Tanning Process—Vacuum Tanning by Pressure without Air. (A)..... 500
TOLMAN, R. C., AND R. S. BRACEWELL, The Molecular Mechanism of Colloidal Behavior. (A)..... 212
TUCKER, F. W., Machine for Stretching Hides. (P)..... 448
TUCKER, F. W., Leather Working Machine. (P)..... 550
TULLY, J. H., Waterproofing Composition. (P)..... 447

VANEY, C., The Biology of the Warble and Means of Exterminating It. (A)..... 543
VEITCH, F. P., The Extraction of Tanning Materials with Different Extractors..... 119
VEITCH, F. P., A Discussion of Methods for the Estimation of Tannin 122
VIE, GEORGES, Synthetic Tannins. (A)..... 249
VIE, GEORGES, Logwood Extracts. (A)..... 251
VIE, GEORGES, Sulphite Cellulose Extracts. (A)..... 433

WHITNEY, R. F., Leather Making Machine. (P)..... 550
WILEY, H. W., AND W. H. KRUG, A Comparison of the International Filter Tube Method and the Official Hide Powder Method..... 51
WILSON, J. A., Hydration as an Explanation of the Neutral Salt Effect 323
WILSON, J. A., Vegetable Tanning as a Colloid-Chemical Process..... 374
WILSON, J. A., The Mechanism of Bating..... 649
WILSON, J. A., AND E. J. KERN, The True Tanning Value of Vegetable Tanning Materials..... 295
WILSON, J. A., AND E. A. GALLUN, The Retardation of Chrome Tanning by Neutral Salts..... 273
WINKLER, L. W., Determination of Sulphuric Acid. (A)..... 601
WINKLER, L. W., Determination of Chromic and Polychromic Acids. (A) 602
WRIGHT, R., The Determination of Moisture in Leather. 1920 Committee Report..... 529
WRIGHT, W. C., Machine for Leather Flexing and Tempering. (P).. 218

YOCUM, J. H., Report on Tannins.....13, 25
YOCUM, J. H., Notes on the Points of Error in the Shake Method of Determining Tannin by Hide Powder..... 12a

ZDANOWSKI, M. A., Method of Making Glazed Kid Leather. (P).... 646
ZDANOWSKI, M. A., Method of Seasoning Leather. (P)..... 647
ZIMMER, F., Zapon and Zellon Lacquers and Their Solvents. (A).... 678
ZIMMERMANN, K., Leather Splitting Machine. (P)..... 336

SUBJECT INDEX

Acacia, The Tannins of the—. W. Moeller. (A)..... 215
Acidity of Ash-Free and of Commercial Gelatine. H. E. Patten and T. O. Kellems. (A)..... 632
Adsorption of Acids and Alkalies by the Protein Molecule, The Chemical Nature of the—. R. S. Bracewell. (A)..... 212
Adsorption of the Constituents of Chrome Liquor by Hide Substance, The Time Factor in the—. A. W. Thomas, M. E. Baldwin and M. W. Kelly..... 147
Adsorption of Chromic Sulphate by Hide Substance, The Time Factor in the—. A. W. Thomas and M. W. Kelly..... 487
Ash in Leather, Definition of Total—, Committee Report. J. M. Seltzer 130

Digitized by Google

Ash in Leather, Total, Soluble and Insoluble—, Committee Report. J. M. Seltzer 270
Analysis of Commercial Casein, The Proximate—. F. L. Browne. (A) 213
Analysis of Chrome Leather, 1920 Committee Report. L. E. Levi.... 269
Analysis of Lime Liquors, Note on—. F. C. Thompson and W. R. Atkin. (A) 245
Analysis of Lime Liquors I, Committee on Limeyard Control. D. Burton 308
Analysis of Lime Liquors II, Committee on Limeyard Control. W. R. Atkin and W. E. Palmer..... 620
Analysis of Sole Leather; the Determination of Water Soluble Matter by the French and English Methods. M. Jalade. (A)..... 247
Analysis of Sulphonated Oils, 1920 Committee Report. G. W. Schultz 283
Analysis of Sulphonated Oils. Discussion..... 595
Analysis of Tanning Materials, A Modified Shake Method for the—. G. Baldracco and S. Camilla. (A)..... 545
Art of Tanning. C. Krouse. (P)..... 549
Artificial Leather and Products Thereof, Process of Producing—. J. Lynah. (P) 648

Basicity of Chrome Liquors, Effect of Neutral Salts on the—. B. B. Dhavale and S. R. Das. (A)..... 673
Barking Machine. I. Rocic. (P)..... 337
Bating, The Mechanism of—. J. A. Wilson..... 650
Biology of the Warble and Means of Exterminating It. C. Vaney. (A) 543
Bisulphites in Extracts, Determination of—. A. T. Hough. (A).... 644
Book Notice 503
Boric Acid, Modification of the Kjeldahl Method for Crop and Soil Analysis. F. M. Scales and A. P. Harrison. (A)..... 330
By-Laws, Proposal to Change Section 7-A of the—..... 130

Casein, The Proximate Analysis of Commercial—. F. L. Browne. (A) 213
Chamois Leather, The Rational Manufacture of—. (A)..... 646
Chemical Control of Iron Tanning. G. Grasser. (A)..... 630
Chemical Nature of the Adsorption of Acids and Alkalies by the Protein Molecule. R. S. Bracewell. (A)..... 212
Chestnut, On the Value of Planting—. (A)..... 606
Chestnut Extract by the Cardem Process, Drying—. H. M. Cormack. (A) 500
Chestnut Wood, The Extraction of—. C. T. Gayley..... 344
Chrome Leather, Complete Analysis of—, Committee Report. L. E. Levi 269
Chrome Liquors; Preparation, Properties and Composition of One-Bath. (A) 178
Chrome Liquors, Titration of— by the Conductance Method. A. W. Thomas and S. B. Foster..... 510
Chrome Suede Calf, The Manufacture of—. "Nappa." (A)..... 501
Chrome Tanning. L. Houben. (A)..... 252
Chrome Tanning. D. Burton. (A)..... 673
Chrome Tanning, The Retardation of— by Neutral Salts. J. A. Wilson and E. A. Gallun..... 273
Chrome Tanning, Single Bath—. E. Griliches. (A)..... 631
Chromed Hide Powder for Tannin Analysis, The Preparation of Lightly—. G. Baldracco and S. Camilla. (A)..... 544
Chromic Hydroxide, On the Evolution and Oxidation of— in Alkaline Solution. F. Burion and A. Senechal. (A)..... 331
Chromium in Chrome Leather, On the Volumetric Determination of—. Te-Pang Hou 367

Digitized by Google

Chromium in Chrome Liquors by Use of the Immersion Refractometer, Rapid Estimation of—. A. W. Thomas and M. W. Kelly..... 665
Chromium Salts; Tanning. J. B. Blockey. (P)..... 217
Colloidal Behavior, The Molecular Mechanism of— II. R. C. Tolman and R. S. Bracewell. (A)..... 212
Colloidal Behavior, The Molecular Mechanism of— III. R. S. Bracewell. (A)..... 212
Color Determination, Need of a Standard Method for—. T. Blackadder and C. L. Garland..... 181
Coloration of Animal Hides by Means of O-Vanillin and O-Protocatechuic Aldehyde and Tanning with Aldehyde. O. Gerngross. (A) 534
Comparison of the International Filter Tube Method and the Official Hide Powder Method. H. W. Wiley and W. H. Krug..... 51
Composition of Matter for Use as a Leather Substitute. J. W. Matthaei. (P)..... 336
Composition of Matter for Use as a Substitute for Leather and Similar Purposes. G. Christenson. (P)..... 337
Contrasting Effects of Chlorides and Sulphates on the Hydrogen Ion Concentration of Acid Solutions. A. W. Thomas and M. E. Baldwin. (A)..... 330
Contribution to the Study of Unhaired Skins. G. Grasser. (A)..... 675
Corinal, A New Synthetic Tan-Stuff. W. Buckow. (A)..... 603
Corrections 450, 503
Council Meetings 450
Critical Study of the Warble in Reply to the Incorrect Statements of C. Vaney. H. Pericaud. (A)..... 544
Criticism of Baldracco and Camilla's Modification of the Official Method. E. Schell. (A)..... 546

Definition of Total Ash in Leather. Committee Report. J. M. Seltzer 130
Degreasing Apparatus. C. Krouse. (P)..... 550
Deliming, The Speed-Rate of—. G. Grasser. (A)..... 679
Detanning Chrome Leather, Glue, etc. M. C. Lamb. (P)..... 218
Determination of Bisulphites in Extracts. A. T. Hough. (A)..... 644
Determination of Chromic and Polychromic Acids. L. W. Winkler. (A) 602
Determination of Formaldehyde in Solution. R. H. Robinson. (A).. 535
Determination of Glucose in Leather. 1920 Committee Report. J. S. Rogers 411
Determination of Inorganic Impurities in Sulphated Oil. R. Hart.... 404
Determination of Lime in Unhaired Skins. G. Grasser. (A)..... 675
Determination of Molybdenum Value, Simplified Method for the—. R. Lauffmann. (A)..... 435
Determination of Moisture in Leather. 1920 Committee Report. R. Wright 529
Determination of Permeability to Water of Sole Leather. E. Jalade..537, 645
Determination of Sulphate in Sulphonated Oils. E. J. Kern. (A).... 535
Determination of Sulphuric Acid. L. W. Winkler. (A)..... 601
Determination of Sulphuric Acid in Leather. A. W. Thomas..... 504
Determination of Total Saponifiable Matter in Sulphated Oil by Difference. R. Hart 495
Determination of Water in Petroleum and Other Organic Emulsions, A Convenient Method for the—. E. W. Dean and D. D. Stark. (A) 435
Determination of Water Soluble in Leather. 1920 Committee Report. G. L. Terrasse and J. F. Anthes..... 581
Diffusion of Tanning Extracts through Gelatine Jelly and Their Relation to Results Obtained by Wilson and Kern. A. W. Thomas.. 593
Dressing for Leather and Leather Substitutes and Process of Making the Same. A. R. Caldwell. (P)..... 448

Digitized by Google

Dressing for Leather and Painted and Varnished Surfaces. W. O. Harris. (P) 337
Drying Chestnut Extract by the Cardem Process. H. M. Cormack. (A) 500
Drying Patent Leather, Method of—. E. Hintz and H. Schultz. (P) 647
Dyers Formulæ 607
Dyes in the Leather Industry, Some Considerations on the Testing of—. L. J. Matos 553

Effect of Cold Upon Raw Hides and Skins. (A) 601
Effect of Neutral Salts on the Basicity of Chrome Liquors. B. B. Dhavale and S. R. Das. (A) 673
Effects of Glucose and Salts on the Wearing Quality of Sole Leather. (A) 171
Effects of Oils, Grease and Degree of Tannage on the Physical Properties of Russet Harness Leather. R. C. Bowker and J. B. Churchill. (A) 600
Elections 129, 219, 267, 449, 551, 649
Emulsions—Theory and Practice. A. W. Thomas 186
Enamelled or Patent Leather. C. Heyl. (P) 447
Enzyme Action, Unhairing of Hides and Skins by—. C. S. Hollander 477
Epsom Salts in Leather, Committee Report. R. W. Frey 406
Estimation of Sulphide. Committee on Limeyard Control III. J. E. Pickles. (A) 673
Estimation of the Tryptic Activity of Bating Materials. A. W. Thomas 221
Evolution and Oxidation of Chromic Hydroxide in Alkaline Solution. F. Bourion and A. Senechal. (A) 331
Extraction of Chestnut Wood. C. T. Gayley 344
Extraction of Tanning Materials with Different Extractors. F. P. Veitch 119
Extraction of Tanning Materials in the Tannery, Practical Method for—. H. Giusiana. (A) 499

Fat in Leather, On the Retention of—. W. Fahrion. (A) 334
Fibrin, The Swelling of— in Alkalies. R. C. Tolman and R. S. Bracewell. (A) 212
Filters, New—. K. Schorlemmer. (A) 600
Foreword 1
Forest Products Laboratory Decennial Celebration 399
Formaldehyde in Leather Manufacture, Use of—. J. Jettmar. (A) .. 644
Formaldehyde in Solution, Determination of—. R. H. Robinson. (A) 535
Formaldehyde in the Tannery. B. Kohnstein. (A) 436
Formol Titration of Hide Powder and Aldehyde Tannage. O. Erngross. (A) 677

Gelatine, On the Swelling of— in Hydrochloric Acid and Caustic Soda. D. J. Lloyd. (A) 640
Gelatine, Note on the Swelling of— in Hydrochloric Acid and Caustic Soda. H. R. Procter. (A) 642
Gelatine Solutions, Acidity of Ash-Free and of Commercial—. H. E. Patten and T. O. Kellems. (A) 632
Gelatine Solutions, Structure of—. F. C. Thompson. (A) 244
Gelatines, Properties and Constitution of Glues and—. R. H. Bogue. (A) 632
Glazed Kid-Leather, Method of Making—. M. A. Zdanowski. (P) .. 646
Glucose, Effects of— and Salts on the Wearing Quality of Sole Leather. (A) 171
Glucose in Leather, Determination of—. Committee Report. J. S. Rogers 411
Glue, Overheating Reduces Strength of Animal—. (A) 499
Glue and Process for Manufacturing Same. S. B. Henning. (P) 337

Digitized by Google

Hemlock Reds. J. N. Hurty 15a
Hemlock Sole Leather—An Historical American Product. (A) 331
Hide Stretcher. A. Berg. (P) 550
Hide Substance. G. L. Terrasse 608
Hides and Skins, Effect of Cold upon Raw—. (A) 601
Hydration as an Explanation of the Neutral Salt Effect. J. A. Wilson 308
Hydrocarbon Tannage. W. Moeller. (A) 214
Hydrogen and Hydroxyl Ion Concentrations of Some Acids and Bases, Tabulation of—. A. W. Thomas 133

Industrial Uses for the Shark and Porpoise. A. Rogers 241
Insolubles in Tanning Extracts, Nature of the—. A. T. Hough. (A) 645
Invention, Research, Engineering, Manufacture. Buckner Speed 516
Iron Salts, Notes upon Tanning with—. V. Casaburi. (A) 176
Iron Tanning, Chemical Control of—. G. Grasser. (A) 630

Lactic Acid Industry. (A) 438
Lacquers, Zapon and Zellon— and Their Solvents. F. Zimmer. (A) .. 678
Leather. C. R. Reubig and O. M. Seemann. (P) 337
Leather, Artificial—. A. A. Somerville. (P) 448
Leather, Artificial—. G. Miller. (P) 549
Leather and Glue. F. C. Thompson 380
Leather Belting, Uses for Waste Ends of—. F. R. Parsons. (A) 629
Leather Compositions. W. Drury. (P) 338
Leather Dyeing. F. Kohl. (A) 444
Leather for Analysis, The Sampling and Preparation of Sole and Harness. Preliminary Committee Report. F. H. Small 475
Leather Graining, Boarding or Softening Machine. J. E. Spencer. (P) 337
Leather Greases in the Years 1914-1918. Smaic and Wladika. (A) .. 676
Leather in the British Engineering Trades. F. R. Parsons. (A) 245
Leather Making. C. Bernard. (P) 648
Leather Making. J. H. Farrar. (P) 648
Leather Measuring Machines. F. J. Schlink. (A) 599
Leather, Method of Treating Varnished (Patent)—. H. Schulz. (P) 218
Leather Paring Machine. J. Loose. (P) 646
Leather Skiving Machine. C. O. Terry. (P) 448
Leather Splitting Machine. K. Zimmermann. (P) 336
Leather Substitute. J. D. Prince. (P) 448
Leather Waste, Utilization of—. A. Harvey. (A) 631
Leather Working and Like Machines. A. Seymour-Jones. (P) 217
Leather Working Machine. F. W. Tucker. (P) 550
Leather Working Machine. R. F. Whitney. (P) 550
Leathers, Substitute—. (P) 447
Lignone, Compounds; Tanning Agents. (P) 549
Lime Liquors, Note on the Analysis of—. F. C. Thompson and W. R. Atkin. (A) 245
Lime Liquors, The Analysis of— I. Committee on Limeyard Control. D. Burton 308
Lime Liquors, The Analysis of— II. Committee on Limeyard Control. W. R. Atkin and W. E. Palmer 620
Liming, Modern Methods of—. (A) 673
Liming Process, Nature of the—. E. Stiasny. (A) 172
Logwood Extracts. Georges Vie. (A) 251
Lyotrope Influence and Adsorption in the Theory of Wetwork. H. G. Bennett. (A) 437

Machine for Leather Flexing and Tempering. W. C. Wright. (P) .. 218
Machine for Seasoning or Finishing Leather. J. U. Flanagan. (P) .. 648

Digitized by Google

Machine for Skiving Leather. C. A. Hirth. (P) 647
Machine for Stretching Hides. F. W. Tucker. (P) 448
Machine for Treating Hides and Skins. D. Mercier. (P) 647
Magnesium Sulphate in Vegetable Tanned Leather and Its Effect upon Analytic Results. E. Jalade. (A) 674
Manufacture of Chrome Suede Calf. "Nappa." (A) 501
Manufacture of Leather. W. C. Blatz. (P) 337
Measurement of the Plumping Power of Solutions. A. A. Claflin 234
Mechanism of Bating, The—. J. A. Wilson 650
Meeting of the I. A. L. T. C. 1901, Report on—. W. H. Krug 75
Meeting of the Section of Leather Chemistry of the A. C. S. 339, 552
Method of Making Glazed Kid-Leather. M. A. Zdanowski. (P) 646
Method of Seasoning Leather. M. A. Zdanowski. (P) 647
Methods for the Estimation of Tannin, A Discussion of—. F. P. Veitch 122
Mimosa Bark and Extract. "Natal." (A) 547
Mimosa Bark and Extracts, Sugar in—. A. Harvey. (A) 245
Mocha Leather, Manufacture of—. L. Forse. (P) 550
Modern Methods of Liming. (A) 673
Modified Shake Method for the Analysis of Tanning Materials. G. Baldracco and S. Camilla. (A) 545
Moisture in Leather, The Determination of—. Committee Report. R. Wright 529
Molecular Mechanism of Colloidal Behavior. II. The Swelling of Fibrin in Alkalies. R. C. Tolman and R. S. Bracewell. (A) .. 212
Molecular Mechanism of Colloidal Behavior. III. The Chemical Nature of the Adsorption of Acids and Alkalies by the Protein Molecule. R. S. Bracewell. (A) 212
Molybdenum Value, Simplified Method for the Determination of—. R. Lauffmann. (A) 435

Nance Tanning Process—Vacuum Tanning by Pressure Without Air. U. J. Thuau. (A) 500
Nature of Quebracho Tannin. W. Moeller. (A) 678
Nature of the Liming Process. Edmund Stiasny. (A) 172
Nature of the Insolubles in Tanning Extracts. A. T. Hough. (A) .. 645
Need of a Standard Method for Color Determination. T. Blackadder and G. L. Garland 181
Neutral Salt Effect, Hydration as an Explanation of—. J. A. Wilson 323
Neutralization of Sulphonated Oils with Ammonia, Soda and Potash. C. G. Bumcke. (A) 672
Nitrification of Leather and Oil Cake, Study of—. R. Guillin. (A) .. 534
Note on the Detection of Sulphite Cellulose in Tanning Extracts. G. F. Knowles. (A) 245
Notes on the Work of Baldracco and Camilla on the Shake and Filter Method. R. Lauffmann. (A) 645
Notice 220

Oil Tannage. W. Moeller. (A) 214, 676
Oiling of Leather, Theory of the Processes in the—. W. Moeller. (A) 176
Order of Diffusion of Tanning Extracts through Gelatine Jelly and Their Relation to Results Obtained by Wilson and Kern. A. W. Thomas 593
Overheating Reduces Strength of Animal Glue. (A) 499

Digitized by Google

Patent Leather, Method of Drying—. E. Hintz and H. Schulz. (P).. 647
Pimenta Officinalis, Tanning Value of the Leaves of—. (A)..... 434
Planting Chestnut, On the Value of—. (A)..... 606
Plumping Power of Solutions, The Measurement of the—. A. A. Claflin 234
Practical Method for the Extraction of Tanning Materials in the Tannery. H. Giusiana. (A)..... 499
Preparation of Lightly Chromed Hide Powder for Tannin Analysis. G. Baldracco and S. Camilla. (A)..... 544
Preparation of Tanning Extracts for Analysis. R. H. Forbes..... 21
President's Address to the Seventeenth Annual Meeting. R. W. Griffith 341
Problems in Leather Making, Some Unsolved—. J. R. Blockey. (A) 444
Process of Dampening Leather. F. J. Blatz. (P)..... 648
Process of Making Leather. A. Rogers. (P)..... 647
Process of Producing Artificial Leather and Products Thereof. J. Lynah. (P) 648
Process of Producing Tannate of Lime Compound Difficultly Soluble in Dilute Acids. R. Tambach. (P)..... 648
Process of the Production of Tanning Extract from Waste Sulphite Lye. Hans Brun. (P)..... 336
Process of Treating Leather. A. J. Hawkins. (P)..... 336
Progress in Tanning in the Year 1918. R. Lauffmann. (A)..... 254
Properties and Constitution of Glues and Gelatines. R. H. Bogue. (A) 632
Proposal to Change Section 7-A of the By-Laws..... 130
Proteids from Waste Liquors of the Hide Treating Art, Recovery of—. C. L. Peck. (P)..... 647
Proximate Analysis of Commercial Casein. F. L. Browne. (A).... 213
Purification of Tannery Wastes. H. B. Hommon. (A)..... 441
Pyroxylin Composition and Process of Making Same. W. F. Doerflinger. (P) 218

Quebracho Tannin. The Nature of—. W. Moeller. (A)..... 678

Rapid Estimation of Chromium in Chrome Liquor by Use of the Immersion Refractometer. A. W. Thomas and M. W. Kelly... 665
Recovering Chrome Salts from Old One-Bath Chrome Liquors. H. Giusiana. (A) 499
Report of Committee on Recommendations in Relation to Methods for Analysis of Tanning Materials..... 12
Retardation of Chrome Tanning by Neutral Salts. J. A. Wilson and E. A. Gallun 273
Retention of Fat in Leather. W. Fahrion. (A)..... 334
Russet Harness Leather, Effects of Oils, Greases and Degree of Tannage on the Physical Properties of—. R. C. Bowker and J. B. Churchill 600

Sampling and Preparation of Sole and Harness Leather for Analysis. Preliminary Committee Report. F. H. Small..... 475
Sant Grains. (A) 434
Science Applied to the Leather Industry. L. Egléne. (A)..... 176
Scrap Leather, Utilizing—. S. C. Lansdown. (P)..... 337
Seasoning Leather, Method of—. M. A. Zdanowski. (P)..... 647
Seasoning and Finishing Leather, Machine for—. J. U. Flanagan. (P) 648
Seventeenth Annual Meeting.....221, 268, 401
Shake Method of Determining Tannin by Hide Powder, Notes on the Points of Error in the—. J. H. Yocum..... 12a

Digitized by Google

Shake Method and Filter Method in the Analysis of Tanning Materials with Hide Powder. G. Baldracco and S. Camilla..... 201
Shark and Porpoise, Industrial Uses for—. A. Rogers..... 241
Silica, Tanning with—. A. T. Hough. (A)..... 174
Sixth National Exposition of Chemical Industries..... 400
Soaking of Hides and Skins. (A)..... 548
Sodium Sulphite and Sodium Bisulphite in the Tannery, Use of—. B. Kohnstein. (A)..... 674
Sole Leather, Determination of the Permeability to Water of—. E. Jalade. (A)..... 537, 645
Sole Leather Tanning, Modern—. L. Houben. (A)..... 644
Some Considerations on the Testing of Dyes in the Leather Industry. L. J. Matos..... 553
Some Observations on the Determination of the True Tanning Value of Extracts According to Wilson and Kern. G. W. Schultz and T. Blackadder..... 654
Some Unsolved Problems in Leather Making. J. R. Blockey. (A).. 444
Speed-Rate of Deliming. G. Grasser. (A)..... 679
Spent Wattle Bark. (A)..... 435
Splits, Some Methods of Utilizing—. (A)..... 629
Staining of Leather or Skins. M. Poto. (P)..... 646
Stretching by Tension. E. Durio. (P)..... 447
Structure of Gelatine Solutions. F. C. Thompson. (A)..... 244
Sugars in Mimosa Bark and Extracts. A. Harvey. (A)..... 245
Sulphate in Sulphonated Oils, The Determination of—. E. J. Kern. (A) 535
Sulphated Oils, The Determination of Inorganic Impurities in—. R. Hart..... 404
Sulphated Oils, The Determination of Total Saponifiable Matter by Difference. R. Hart..... 495
Sulphide, Estimation of—. Committee on Limeyard Control III. J. E. Pickles. (A)..... 673
Sulphite Cellulose Extracts. Georges Vié. (A)..... 433
Sulphite Cellulose in Tanning Extracts, Note on the Detection of—. G. F. Knowles. (A)..... 245
Sulphonated Oils, The Analysis of—. Committee Report. G. W. Schultz..... 283
Sulphonated Oils, The Analysis of—. Discussion..... 595
Sulphonated Oils, The Commercial Examination of—. G. F. Pickering. (A)..... 630
Sulphonated Oils, The Neutralization of— with Ammonia, Soda and Potash. C. G. Bumcke. (A)..... 672
Sulphuric Acid in Leather, The Determination of—. A. W. Thomas.. 504
Swelling of Gelatine in Hydrochloric Acid and Caustic Soda, On the—. D. J. Lloyd. (A)..... 640
Swelling of Gelatine in Hydrochloric Acid and Caustic Soda, Note on the—. H. R. Procter. (A)..... 642
Swelling of Limed and Hydrated Hide in the Presence of Acid or Alkali. G. D. McLaughlin..... 228
Swelling and Falling of White Hide in Vegetable Tan Liquors. G. D. McLaughlin and R. E. Porter..... 557
Synthetic Tanning-Agents. M. Melamid. (P)..... 338
Synthetic Tanning-Agents. A. G. Bloxam. (P)..... 447
Synthetic Tanning-Agents. A. Koetzle. (P)..... 549
Synthetic Tannins. Georges Vié. (A)..... 249
Synthetic Tannins and Their Use in the Tannery. E. Nihoul..... 156

Digitized by Google

Tabulation of Hydrogen and Hydroxyl Ion Concentrations of Some Acids and Bases. A. W. Thomas 133
Tan Barks of Western Australia. (A) 434
Tannery Wastes, The Purification of—. H. B. Hommon. (A) 441
Tannin Analysis. J. Jedlicka. (A) 216
Tannin, Report on—. W. H. Krug 2
Tannin, Report on—. J. H. Yocum 13, 25
Tannin, Report on—. Oma Carr 41
Tannin, Report on—. W. K. Alsop 54
Tannin, Report on—. W. T. Teas 78
Tannin, Report on—. G. A. Kerr 87, 95
Tanning. W. Clark. (P) 338
Tanning, (P) 549, 648
Tanning Agents, Lignone Compounds. (P) 549
Tanning Chemistry and Technique in 1919. R. Lauffmann. (A) 680
Tanning Compound. B. Levin. (P) 218
Tanning Extract from Waste Sulphite Lye, Process of the Production of—. H. Brun. (P) 336
Tanning Industry in Spain. (A) 536
Tanning Leather for Belts. F. Gilardini. (P) 218
Tanning Material and Method of Producing the Same. A. Koetzle. (P) 550, 646
Tanning Material from Waste Sulphite Liquor. (A) 171
Tanning Process. J. M. Brown. (P) 218
Tanning Value of the Leaves of Pimenta Officinalis. (A) 434
Tanning Wastes, Agricultural Utilization of—. B. Fallot. (A) 534
Tanning with Aldehyde. O. Gerngross. (A) 534
Tanning with Iron Salts, Notes upon—. V. Casaburi. (A) 176
Tanning with Silica. A. T. Hough. (A) 174
Tannins from Wattle Bark. W. McGlynn, F. A. Coombs, et al. (A) 604
Tannins of the Acacia. W. Moeller. (A) 215
Tannins, Synthetic— and Their Use in the Tannery. E. Nihoul 156
Theory of the Processes in the Oiling of Leather. W. Moeller. (A) 176
Theory of Leather Formation. W. Fahrion. (A) 677
Time Factor in the Adsorption of the Constituents of Chrome Liquor by Hide Substance. A. W. Thomas, M. E. Baldwin and M. W. Kelly 147
Time Factor in the Adsorption of Chromic Sulphate by Hide Substance. A. W. Thomas and M. W. Kelly 487
Titration of Chrome Liquors by the Conductance Method. A. W. Thomas and S. B. Foster 510
Total, Soluble and Insoluble Ash in Leather. Committee Report. J. M. Seltzer 270
Treating Leather. O. Röhm. (P) 217
Treatment of the Warble. H. Pericaud. (A) 433
True Tanning Value of Extracts According to Wilson and Kern, Some Observations on the Determination of—. G. W. Schultz and T. Blackadder 654
True Tanning Value of Vegetable Tanning Materials. J. A. Wilson and E. J. Kern 295
True Tanning Value of Vegetable Tanning Materials. Discussion 451
Tryptic Activity of Bating Materials, Estimation of—. A. W. Thomas 221

Digitized by Google

Unhairing of Hides and Skins by Enzyme Action. C. S. Hollander.. 477
Use of Formaldehyde in Leather Manufacture. J. Jettmar. (A).... 644
Use of Sodium Sulphite and Sodium Bisulphite in the Tannery. B. Kohnstein. (A) 674
Uses for Waste Ends of Leather Belting. F. R. Parsons. (A)..... 629
Utilization of Leather Wastes. A. Harvey. (A)..... 631
Utilization of Tanning Wastes, Agricultural—. B. Fallot. (A)..... 534
Utilizing Scrap Leather. S. C. Lansdown. (P)..... 337
Utilizing Splits, Some Methods of—. (A)..... 629

Vacuum Tanning by Pressure Without Air—The New Nance Tanning Process. U. J. Thuau. (A)..... 500
Vegetable Tanning; Chemical and Theoretical Considerations. C. Schiaparelli. (A) 253
Vegetable Tanning as a Colloid-Chemical Process. J. A. Wilson..... 374
Vegetable Tanning Matter, What Do We Really Determine as—. E. Schell 669
Volumetric Determination of Chromium in Chrome Leather. Te-Pang Hou 317

Warble, A Critical Study of the— in Reply to the Incorrect Statements of C. Vaney. H. Pericaud. (A)..... 544
Warble, The Biology of and Means of Exterminating It. C. Vaney. (A) 543
Warble, The Treatment of the—. H. Pericaud. (A)..... 433
Water in Petroleum and Other Organic Emulsions, A Convenient Method for the Determination of—. E. W. Dean and D. D. Stark. (A) 435
Water Soluble in Leather, The Determination of—. Committee Report. G. L. Terrasse and J. F. Anthes..... 581
Water Soluble Matter by the French and English Methods, The Determination of—. M. Jalade. (A)..... 247
Waterproofing Composition. J. H. Tully. (P)..... 447
Wattle Bark, Tannins from—. W. McGlynn, F. A. Coombs, et al. (A) 604
Wearing Quality of Sole Leather, Effects of Glucose and Salts on the—. (A) 171
What Do We Really Determine as Vegetable Tanning Matter. E. Schell 669

Zapon and Zellon Lacquers and Their Solvents. F. Zimmer. (A)... 678

ARTICLES FROM OTHER PUBLICATIONS

(Page numbers without titles denote abstracts)

Annual Reports of the Society of Chemical Industry—
Leather and Glue 380
Bureau of Standards Technologic Papers.....599, 600
Chemical Abstracts 630
Chemical Age 438
Chimie et Industrie—
Synthetic Tannins and Their Use in the Tannery..... 156
Collegium.....214, 600, 601, 602, 603, 674, 675, 676, 677, 678, 679
Commerce Reports 536
Commonwealth of Australia, Science and Industry..... 604
Experiment Station Record 534
Gerber.....176, 178, 215, 216, 254, 334, 444
Gerber-Courier 548
Journal American Chemical Society.....212, 330
Hydration as an Explanation of the Neutral Salt Effect..... 323

Digitized by Google

Journal of Industrial and Engineering Chemistry.....213, 330, 435, 535
The True Tanning Value of Vegetable Tanning Materials..... 295
The Mechanism of Bating..... 650
Journal Society of Chemical Industry.....435, 534, 630, 631, 632
Industrial Uses for the Shark and Porpoise..... 241
Journal Society of Leather Trades Chemists.....172, 244, 245, 434, 435 437, 545, 640, 642, 673.
The Shake and Filter Method in the Analysis of Tanning Materials with Hide Powder..... 201
Committee on Limeyard Control. I. The Analysis of Lime Liquors 308

Committee on Limeyard Control. II. The Analysis of Lime Liquors 620
Leather Trades Review 436
Leather World.....547, 629, 631, 673
Le Cuir.....174, 176, 247, 249, 251, 252, 253, 331, 433, 499, 500, 537, 543 544, 545, 546, 644, 645, 674
What Do We Really Determine as Vegetable Tanning Matter.. 669
Ledertechnische Rundschau.....606, 645, 646, 680
Public Health Bulletins of U. S. Public Health Service..... 441
Shoe and Leather Reporter.....245, 331, 444, 672

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NOTICE

The following articles, pages 1a to 19a, should precede the first article in the January number of the JOURNAL. In connection with the plan to publish all of the experimental, collaborative work of the Association, previous to the publication of our JOURNAL, this should have been published in the January number but was omitted through an oversight. However, in assembling the JOURNALS for the year, for binding, these articles should be placed before the first article in the January number so that they will be in the proper chronological order.

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REPORT ON TANNIN.

By W. H. Krug.

Proceedings of the Association of Official Agricultural Chemists for 1894.

The Congress of Chemists held in conjunction with the Columbian Exposition at Chicago last year, brought together a large number of prominent chemists, among whom were several that are connected with the leather trade. I was at that time engaged at the exhibit of the Chemical Division in the Government building in an investigation of the foreign tanning materials which were exhibited at the Exposition. This work was undertaken for the Forestry Division of the Department of Agriculture, and it was desired to show the practical value of these materials. For this purpose I used the method recommended by Procter in England, which is known to all of you and consists in percolating the liquid through a column of hide powder and determining the solids remaining in the percolate after rejecting the first 50 cc. I was assisted in this work by Prof. Collingwood, of the Arizona Experiment Station, and neither of us was satisfied with the method.

In conjunction with Mr. Hurty and Mr. Westenfelder we extensively discussed the subject, and fully realizing the importance of having a uniform method which, even if not giving absolute results, would at least yield such as were concordant and comparable, we decided to attempt a realization of this. In accordance with this decision a meeting was called for the 30th of October at the rooms of the Chicago Academy of Sciences, and invitations were sent to a number of tanning chemists. Owing to the distance that separates Chicago from the East, where many of these chemists are located, none of the Eastern chemists could be present, but all sent answers expressing manifest pleasure in the fact that such work was to be undertaken and promising their hearty co-operation. Messrs. Hurty, Fiebing, Westenfelder, and myself were present, and after long discussion decided to organize the Association of American Leather Chemists and drafted a provisional method, as follows:

Provisional Method.

1. Use such an amount of extract that 100 cc. of the solution shall contain about 1 gram of dry solids.

2. Add to the extract taken about 200 cc. of water at or over 80° C., stir until dissolved, transfer to a graduated flask, washing out the beaker with warm water, cool and make up to the mark. Shake thoroughly, immediately take 100 cc., evaporate, dry to constant weight at 95 to 100° C., and weigh. Result is total solids. Now filter the remainder of the solution through thick filter paper 9 cm. in diameter (S. and S. sirup filter paper is recommended), using a teaspoonful of purified kaolin if necessary. Take 100 cc. of filtrate, evaporate and dry for total soluble matter.

Note.—The dishes should be covered during drying, so as to prevent loss by popping, and the residues must always be dried to constant weight, at a temperature not exceeding 100° C.

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3. Determine the amount of soluble matter in the hide powder by making a blank analysis identical with the method used for determining the tannin.

4. Take 6 grams of hide powder, put into a glass with 100 cc. of water, and shake for five minutes. This will remove traces of soluble matter. Strain through well-washed muslin or linen, and squeeze out very thoroughly.

Divide the moist hide powder into three portions. Take about 130 cc. of filtered tannin liquid and shake up with the first portion of hide powder for about five minutes. Strain through well-washed muslin or linen. To the strained liquid add the second portion of hide powder, shake again for five minutes and strain as before. To the filtrate add the last portion of hide powder and shake again for about eight minutes. Now filter through sirup filter paper pouring the liquid back if necessary, so as to obtain a perfectly clear filtrate. Take 100 cc. of the filtrate, evaporate, and dry as before.

(*a*) It is absolutely necessary to use some form of mechanical shaker, as shaking by hand is not intense enough to remove all the tannin. The association recommends any form of the machine known as "milkshaker."

5. Determine the moisture in the extract by drying 2 grams to constant weight.

The method of investigation used by the Association of Official Agricultural Chemists was adopted. This consists in sending to each chemist who is to participate in the work a sample of the substance to be analyzed, together with a minute description of the method to be used. This method is to be closely followed, and the results sent in to the reporter, who tabulates them and draws his comparisons. Uniform samples of extract and hide powder were accordingly sent to the following chemists: Messrs. Hurty, Adriance, Fiebing, Trimble, Westenfelder, Yocum, Collingwood, Kerr, Norris, Trubek, and the Tiffany Chemical Company.

Reports were received from nine chemists.

TABLE OF RESULTS.

Analyst	Total solids Per cent.	Soluble solids Per cent.	Tanning Subst. Per cent.	Total solids by direct Method Per cent.
J. H. Hurty	42.74	41.91	24.88	—
B. D. Westenfelder	41.72	41.22	26.21	42 05
J. H. Fiebing	41.60	40.60	23.20	—
H. Trimble	44.32	41.84	*24.90	43.32
W. M. Norris	43.55	40.67	25.75	—
J. S. Adriance	42.98	40.48	23.69	—
J. H. Yocum	43.75	41.66	27.50	—
C. A. Kerr	42.85	41.66	25.20	—
W. H. Krug	41.63	40.46	23.36	42.29
Mean	42.693	41.164	24.974	42.553
Difference between maximum and minimum	2.72	1.45	4.30	1.27

*Mr. Trimble's result excluded from the average, not having been obtained by the provisional method.

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Analyst	Residues in grams
J. H. Fiebing	0.008
W. M. Norris	0.0149
J. S. Adriance	[2]0.0043
J. H. Yocum	0.040

[2] This was calculated from result on 5 grams, which was stated to be 0.0715 per cent.

The individual reports differed in so many details that they could not be compiled into one table, and are therefore given below. Mr. Westenfelder, Cincinnati, sends the following report:

TABLE I.

	Total Solids Per cent.	Water by difference Per cent.	Total Ext. Per cent.	Sol. Ext. Per cent.	Insol. Ext. Per cent.	Non-Tannins Per cent.	Tannins Per cent.
	42.05	57.95	41.72	41.22	0.50	14.96	26.26
	—	—	—	—	—	15.06	26.16
Mean:	42.05	57.95	41.72	41.22	0.50	15.01	26.21

TABLE II.—DETERMINATION OF NON-TANNINS WITHOUT WASHING THE HIDE POWDER.

	Non-tannins Per cent.	Tannins Per cent.	Soluble extract by addition Per cent.
	16.87	24.35	41.22
	19.13	22.09	41.22
Mean:	18.00	23.22	—

Tannin by Lowenthal method, using hide powder to remove the tannin = 25.82 per cent.

He writes: "The sample of extract was in a high state of fermentation, which I think will not materially influence the results of tannin, but will lower the figures for solids and non-tannins and increase the proportion of tannin to total extractive matter. Please observe that I have given two results for non-tannins and tannins. Results in Table I agree, and in Table II disagree. I account for this that I shook No. 2 more violently, thereby causing more soluble matter. At any rate, I can see that if the hide powder is not first washed with water the results will vary as much as by the old filter tube method. As to the results by the Lowenthal method, I will say that I proceeded rather differently from the recommendation given by the German Association of Tanning Chemists. Instead of macerating the hide powder in the liquid for twenty-four hours, I shook up the hide powder in a flask with water, put a plug of absorbent cotton in the neck of a funnel, poured the magma on it, and thoroughly washed it with water. After draining well I poured the liquid upon it and diiscarded

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about 50 cc. of the filtrate. The filtrate following was used for titration. I used about 3 grams of hide powder."

Mr. Fiebing, Milwaukee, sends this report:

(1) MR. FIEBING'S RESULTS:

Extract per liter Grams	Total solids Per cent.	Total soluble solids Per cent.	Insoluble matter Per cent.	(a) Non-tannins without correction for water in the hide powder Per cent.	(b) Non-tannins with correction for water in the hide powder Per cent.
24.759	41.6	40.7	0.90	17.2	19.2
24.965	41.6	40.5	1.10	17.6	19.3
Mean:	41.6	40.6	1.00	17.4	19.25

(c) Non-tannins by filter method Per cent.	(d) Non-tannins by shaking with dry hide powder Per cent.	(e) Non-tannins by filter method using different hide powder Per cent.	(f) Non-tannins by shaking 24 minutes with total hide powder Per cent.	6 grams hide powder contain soluble matter Per cent.	6 grams hide powder retain after pressing Gram water Grams
17.5	19.20	—	—	0.008	14.0
17.5	—	17.9	19.5	—	12.0
17.5	19.20	17.9	19.5	0.008	13.0

(2) Tannins calculated from the above results.

a. Per cent.	b. Per cent.	c. Per cent.	d. Per cent.	e. Per cent.	f. Per cent.
23.20	21.35	23.10	21.40	22.70	21.10

Mr. Trimble, Philadelphia, sends the following report:

	Total Solids Per cent.	Moisture direct Per cent.	Insoluble matter Per cent.	Soluble extract Per cent.	Tannins Per cent.
	44.43	56.68	2.52	41.91	24.88
	44.21	—	2.44	41.77	24.91
Means:	44.32	56.68	2.48	41.84	24.90

Tannins by the Procter percolation method, rejecting first 80 cc.

Tannins Per cent.
21.68
21.63
Mean: 21.66

He writes: "In every case your suggestions were complied with, except in using a 'milk-shake' apparatus. The hide powder used in the latter method was obtained from Eitner in Vienna."

William M. Norris, New York, writes: "S. and S. paper No. 591 was used in filtering."

John H. Yocum, New York, sends the following report:

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Moisture direct Per cent.	Total extract Per cent.	Sum of extract and Moisture Per cent.	Insoluble matter Per cent.	Non-tannins Per cent.	Tannins Per cent.
56.10	43.75	99.85	2.09	14.16	27.50

METHOD IN USE IN LABORATORY.

Non-tannins Per cent.	Tannins Per cent.
14.52	27.14

Soluble matter in hide powder, 6 g. to 200 cc.

Official H. P. Grams	Laboratory H. P. Grams
0.040	0.081

He writes: "The extract was of necessity kept so long that when opened it was found to have soured. While not thinking this would interfere with the analysis, you should know of it. The method in use in the laboratory is the same as the Association method, the only difference being in the hide powder used, and in a slightly longer time in the extraction. The hide furnished by you gave 0.040 grams to 6 grams in 200 cc. of water treated the same way as in an analysis while that in use in our laboratory gave 0.081 gram in like amount and method. I would suggest an estimation of the nitrogen as a method of determining the soluble matter in the residue due to the hide powder."

Mr. Kerr, Columbus, Ind., sends the following report:

Method	Total extract Per cent.	Soluble extract Per cent.	Insoluble extract Per cent.	Tannins Per cent.	Water direct Per cent.
Provisional Method:					
H. P. from Fiebing.....	42.85	41.66	1.19	25.20	56.57
H. P. from Eitner.....	42.85	41.66	1.19	25.40	56.57
Laboratory Method:					
H. P. from Fiebing.. ...	42.85	41.66	1.19	24.80	56.57
H. P. from Eitner.....	42.85	41.66	1.19	25.10	56.57

From Mr. Kerr's letter I infer that he used the filtering method in his laboratory.

DISCUSSION OF INDIVIDUAL REPORTS.

Mr. Westenfelder sent in three results for tannins obtained by different methods—one by the provisional method, one obtained with an unwashed hide powder, and one obtained by the Lowenthal method. The results with unwashed hide powder are much lower than those obtained by the provisional method, but as the latter are not corrected for the water retained by the hide powder it is uncertain whether this difference is due to the omission of the washing, especially as Mr. Fiebing found a difference of but 0.05 per cent. between the tannins corrected for the retained water and those obtained with unwashed hide powder. The result obtained by Mr. Westenfelder by the Lowenthal method is 0.4 per cent. lower than the provisional method, not an excessive difference.

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Mr. Fiebing sent in a very full report. He obtained almost identical results by the provisional method and the filter method. His work on the water retained by the hide powder shows the importance of a correction for this error, the difference between the uncorrected and corrected tannins being 1.85 per cent. He does not state what hide powder he used in obtaining result E, but it is evident by the difference between this and the figure obtained by the filter method, using the official hide powder (Result C), that the absorptive power of the hides was different, and this is one point which will have to be taken into consideration by the association if it desires to arrive at a satisfactory method. Unfortunately Mr. Fiebing did not make an estimation by the provisional method, using this other hide powder.

Prof. Trimble's report shows the inferiority of the percolation method when compared with the provisional method. It gave a result 3.6 per cent. lower than the latter. Prof. Trimble's work, though not done with a milk shaker, compares very favorably with the work of the other analysts, his mean being almost identical with the mean of the figures obtained by the provisional method.

Mr. Yocum uses a method in his laboratory which is almost identical with the provisional method, the only variation being in a slightly longer time of contact with the hide powder. Strangely enough the figure obtained by this method is slightly lower. This again may be due to the hide powder used, having its origin either in a different retentive or absorptive power.

Mr. Kerr reports analyses made by the provisional and filter methods, using Fiebing's and Eitner's hide powder. In both cases the latter gave a slightly higher figure. The results by the filter method are lower, though this difference is not very great.

Discussion of Results.

In looking at Table No. 1, a compilation of the comparable results, the wide difference between the minima and maxima is immediately evident. In the case of the most important estimation, the tannins, it is absolutely startling and seems beyond explanations.

Various reasons may be advanced for these variations. In the case of the total extract the manner of taking the sample is liable to lead to erroneous results.

Unless an extract is carefully manufactured it often contains material which, even after shaking violently, settles to the bottom before the analyst can take out a uniform sample with the pipette. The fact that several of the analysts allowed some time to elapse before analyzing the sample, so that it was partially fermented, does not seem to have had a tendency to uniformly lower the figure for total extract. Messrs. Westenfelder, Norris and Yocum reported the sample fermented. The former obtained 41.72 per cent. total extract, the two latter 43.55 and 43.75 per cent. respectively. The least difference between results is found in the column "soluble extract." The only cause for any difference which can be ad-

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vanced outside of the destructive influence of fermentation is imperfect filtration. I have found this part of the work quite unsatisfactory. The diluted extract at first filters very rapidly; then the paper becomes clogged, and it takes hours to obtain the quantity requisite to operate with. I think that great improvement may be made at this point. A few analysts sent in reports on the amount of soluble matter in the hide powder treated by the provisional method. They vary so much, however, that it is impossible to explain the variation. The greatest variation is found in the column "Tannins". Various reasons have suggested themselves in explanation of this. They are as follows:

First. The length of time the extract stood in the laboratory before being analyzed. In several cases the analysts reported the sample fermented; in others the fermentation may have commenced, and I do not doubt for a moment that the changes brought by such fermentation materially affected results.

To test this I analyzed a sample of the extract in July, three months after my first analysis had been made. The sample had stood all this time in a warm place, and the cork was almost driven out by the gases generated during decomposition. On pouring out the extract it was found to be quite thin, whereas the original sample was thick. I obtained the following results:

	Total extract Per cent.	Soluble extract Per cent.	Tannins Per cent.
Original analysis	41.63	40.46	23.36
Second analysis	39.83	39.60	21.68
Difference	1.80	0.86	1.68

It is therefore evident that this fermentation does affect the tannins, and we may here seek an explanation for the wide differences exhibited in the table.

Second. Thoroughness with which the diluted extract was mixed with the hide powder, or, in other words, the speed at which the milk shaker is run. This seems to me an important point. The great objection to all previous methods of determining tannin, based on treatment with hide powder, has always been that the liquor did not come in sufficiently thorough contact with the powder to extract all the tannins. The treatment in the "milk shaker" is a most important step towards "eliminating" this objection, but even here a difference in the violence with which the mixture is shaken up must cause some variation.

Third. The amount of water retained by the hide powder after washing and expressing. This is most certainly a source of error, as shown by the results sent in by Mr. Fiebing. His figures show a difference of almost 2 per cent. between the results directly determined and those corrected for the water retained by the hide powder. When the hide powder is expressed as directed in the provisional method it is certainly

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impossible to obtain a uniform retention of water. The statement "squeeze out thoroughly" is, at the best, indefinite, and there will in most cases be a difference of opinion among analysts as to when this is accomplished. I think that the method used by Mr. Fiebing, namely, to squeeze in a copying press, will do much towards diminishing the possibilities of error from this source. The water retained by the hide powder when squeezed can be determined once for all for each batch of hide powder, and this factor applied as the variation between individual determination when the full pressure of the press is applied is no doubt too small to materially affect the correction.

Fourth. The method of drying the residues. It has been the universal experience in our laboratory that it was well-nigh impossible to arrive at an accurate estimate of the total solids in solutions of organic substances by the direct method. By the direct method, we understand drying in an oven at 100 C. until constant weight is obtained. I say "well-nigh impossible," and might say impossible, because we have never found a substance of this kind that could be dried to constant weight. The determination of the moisture has been the subject of discussion and experimentation in the Association of Official Agricultural Chemists for many years. All methods of drying have been exhaustively tried by this association, among which may be named, for solids, drying in hydrogen at 100° and drying in air at 100°; for liquids, drying in air, in open dish, at 100°, drying in vacuo at 110°, film drying, etc. The great difficulty with all these is the impossibility of obtaining a constant weight. The samples will lose up to a certain point, and from there on rapidly gain. In experiments made in our laboratory on samples of molasses, with the method of drying in an open dish at 100°, the samples were still losing weight after having been dried one hundred and sixty-five hours. Appreciating the impossibility to obtain absolute final results which represented the true amount of moisture in samples, the agricultural chemists have always used compromise methods, which at least insured comparable figures. Thus, in feeding stuffs they specify drying in hydrogen at 100° for five hours, the loss to be called the moisture; in sugars, sirups, honeys, etc., to dry until the loss in one hour is not greater than 0.20 per cent. There are two reasons for this inability to obtain a constant weight, namely, decomposition and oxidation. Decomposition may set in and cause a loss which is estimated as moisture, and oxidation may begin at some indeterminable time and render it well-nigh impossible to determine the point where the last loss occurred. Both processes may be going on simultaneously, and the result thereby be thoroughly vitiated. At the meeting in Chicago I brought up this point, but was assured at the time that it was exremely easy to obtain a constant weight. I have found, however, in all my work, both with the official sample of extract and a hemlock extract furnished by Mr. Hurty, that the residues would lose for about five hours and then gain very rapidly.

During the last few months Messrs. Carr and Sanborn, of our division, have made extensive experiments on this subject, with the view of solving

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the problem. It gives me great pleasure to say that they have accomplished this, and, as I am sure that it will interest the association, I will read a letter which they have written at my request and which gives a resume of their work, together with some of the results achieved.

U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF CHEMISTRY,
Washington, D. C., August 21, 1894.

Dear Sir: Replying to your request for a description of the drying method with which we have secured such uniform results on readily decomposable sugar solutions, we beg to transmit the following, adapted to meet what we conceive, from your information, to be the primary difficulties in quantitative desiccation of tanning extract. It is not asserted, much less claimed, that this method is completely satisfactory for the drying of all organic solids in solution. On the contrary, we content ourselves with the belief that it far surpasses any method within our knowledge. We realize very acutely that better results are likely to be obtained by conversion of the decomposable body to be dried into a salt which resists the effect of prolonged heating more completely. In the interim, while researches are under way in the latter direction, we believe it advisable to adopt a method which partially obviates the effect of heating by conducting the drying in a manner which insures maximum rapidity. Drying upon sand, kieselguhr (tripoli), and similar media which depend for their efficiency upon the greatness of heating surface and the division of the drying solution into delicate films, fail because of their tendency to form clots or thick masses which dry very slowly toward the end of the desiccation.

To obviate these difficulties we prepare our drying medium as follows: Good porous pumice stone is broken into pieces (1) approximately 1 cm. square and (2) smaller particles which pass through a sieve having six meshes to the inch, but resist passage through a sieve one size smaller. The smaller particles must be thoroughly freed of dust.

A platinum drying dish of any convenient size may be employed, provided it contains sufficient stone to completely absorb from 5 to 8 cc. of the extract solution. The dish having been prepared by covering the bottom with the fine particles, and these in turn by a layer of the large pieces, the dish and contents are heated to redness for fifteen or twenty minutes, cooled and weighed. The solution is weighed from a tared bottle or flask, and by means of a pipette with a fine nozzle is evenly distributed over the larger pieces of stone. The object in using the fine particles of pumice stone is to prevent the solution from coming in contact with the dish. It is likely, judging from results upon refractory molasses samples, that the drying will be complete at the end of three hours. We would suggest resort to careful checking as to time of drying. If the solution is fairly homogeneous the above weight will suffice.

As an example of the results obtained by the method upon solutions which can not be dried by ordinary methods, we would instance the following upon a prepared solution which contained sucrose, dextrose,

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levulose, tannic acid, gum arabic, and sodic chloride, the theoretical solids being 23.63 per cent.:

Hours Drying	Per cent. solids (a)	Per cent. solids (b)
1	23.87	23.92
2	23.76	23.67
3	23.72	23.66
4	23.70	23.72
5	23.65	23.65
6	23.63	23.64

These results are quoted impartially from a great number obtained on the same solution, and are intended solely to convey an idea of the extreme rapidity of the method, which explains in great part, we believe, the possibility of securing uniform results upon solutions containing high percentages of unstable substances.

Trusting that this method may meet the difficulties now encountered in the examination of tanning extracts, we remain,

Very sincerely yours,

O. CARR,
T. F. SANBORN.

MR. W. H. KRUG, *Reporter.*

The fact that the result depends greatly on the manner of drying has been appreciated by H. R. Procter, one of the most prominent leather chemists in England. In an article published in the *Journal* of the *Society of Chemical Industry*, 11, 329, on the "Technical analysis of tanning materials," he describes his method as follows:

Porcelain dishes, 7.5 cm. in diameter, are recommended, and the residues are to be dried at 110° C. and weighed every ten minutes until constant weight is obtained. For determining the water a separate portion is dried at 110° C. Of block gambier and fluid extracts only 1 gram must be used, and this evenly distributed in a thin layer in the dish."

It is evident that where a chemist is limited in time this method of dryng is very tedious. He will be continually occupied weighing, and when, as in the case of the extract of a canaigre root, which I recently analyzed, it takes eighteen hours before the residue ceases to lose, weighings every ten minutes are very impracticable. In all technical work speedy and time-saving methods are most desirable, and if it is found that by the method of Messrs. Carr and Sanborn we can obtain reliable results we will have attained this.

I do not think it advisable for us to launch into a new method and immediately totally abandon the old. It will be much better to make comparative determinations during the ensuing year, and then at the next meeting settle upon some definite method if the results warrant it. The direct drying of a weighed amount of the extract has its great drawbacks. The extract is thick, and it is difficult to dry it quickly after the

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surface has become covered with a hard film. I therefore suggest in my recommendations a method after the Association method for sweet wines.

It does not seem necessary to me to make a total extract determination in the diluted extract and a separate moisture determination in the undiluted sample. It appears to be an unnecessary duplication of work. Which of these can be omitted can be determined by future work.

In accordance with the above, I make the following recommendations:

1. That in paragraph 4 of the provisional method, "squeezed thoroughly" be changed to "squeeze in a copying or other suitable press until no more water is expressed."

2. That "shake up with the hide powder" be changed to "shake with the hide powder in a milk-shake apparatus at the highest possible speed."

3. That a paragraph be introduced to read as follows: "Determine the water retained in the hide powder and correct for the error caused thereby."

4. That the reporter for the ensuing year be instructed to make comparative determinations of the total solids by the direct method of drying the extract at 100° C., by the direct method of drying, 100 cc. of the diluted extract at 100° C., by the method of Messrs. Carr and Sanborn of drying 10 grams on pumice stone at 100° C. and determining the time required to obtain constant weight and by the following method: "Five grams of the thoroughly mixed extract are weighed into a suitable dish of 200 cc. capacity, diluted with 100 cc. of warm water, evaporated to dryness on the water bath, and dried in an oven at 100° C. until the residue commences to gain in weight."

DETERMINATION ON THE SAME SAMPLE OF HEMLOCK EXTRACT, PROVISIONAL METHOD, BY THE GENTLEMEN NAMED. SAME HIDE POWDER USED BY ALL.

	Solid matter Per cent.	Soluble Solids Per cent.	Insoluble matter Per cent.	Tannin Per cent.	Non-Tannin Per cent.
Fiebing:					
First time	53.80	44.40	9.40	27.40	17.00
Second time	53.80	44.50	9.30	26.20	18.30
Krug	51.62	44.78	6.84	25.34	19.44
Westenfelder:					
First time	54.86	—	—	—	18.17
Second time	53.64	45.58	8.06	27.90	17.68
W. B. Taber	55.45	49.90	5.55	31.30	18.60
Hurty:					
First time	54.65	47.32	7.33	28.41	20.00
Second time	55.03	47.97	7.06	27.38	18.90

5. That the reporter be instructed to experiment with modes of filtration with the view of improving this part of the method.

6. That the Association fix upon some limit for the amount of soluble matter in the hide powder.

7. That the reporter be instructed to experiment with the methods of using the three portions of hide powder without intermediate filtration, and of using all the hide powder at once.

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8. That the reporter be instructed to experiment with different hide powders to determine whether they vary in absorption power. The retentive power must each time be determined and corrected for.

In conclusion, I offer a report by Mr. Hurty on some analyses made by several chemists of the hemlock extract which, he states, gave him considerable trouble. The results vary as widely as those on the official sample, and what I have said in the case of the latter applies to them.

Fiebing's analyses made July 2, 1894. Krug's analyses made July. Westenfelder's analyses made, first one, July 21, 1894; second one, August 3, 1894. Taber's analyses made May, 1894. Hurty's analyses made, first one, June 25, 1894; second one, June 28, 1894.

NOTES ON THE POINTS OF ERROR IN THE SHAKE METHOD OF DETERMINING TANNIN BY HIDE POWDER.

By J. H. Yocum.

The shake modification of the hide-powder method was originated in my laboratory some two years ago, and has been used constantly since that time, the first published account appearing in the *Leather Manufacturer,* in April, 1893. Since then it has been adopted as provisional by this association and quite recently been favorably commented upon by Dr. Procter.

I have made a large number of analyses, 800 or more, by this method, and it has given constant results for tannery work. Its advantages over the filter are less time, less trouble, and availability in a very warm climate, and if not more, certainly fully equal accuracy.

I have endeavored to find the corrections necessary to make the results from this absolute. The corrective points are dilution due to water carried into the analysis by the dampened hide and soluble hide substance getting into the non-tannin filtrate.

The method as used in this laboratory does not essentially differ from the provisional one.

To determine non-tannins in a tannin solution, 150 cc. of the liquor is taken and shaken with nine grams of hide in three portions each shaking lasting ten minutes, filtered through linen the first and second shakings and the last time through paper. The hide is prepared by shaking ten grams of the hide with 200 cc. water for ten minutes and throwing on a filter; it is then squeezed and the surplus water removed. This is best done in a press where the same pressure can be obtained each time. About three grams of the wet hide is dried to determine the moisture, equal to about one gram of dry and the balance used for the analysis as above. By this method of procedure six grams of hide powder are used to extract 100 cc. of the tannin solution, and the shaking having lasted for thirty minutes in all the tannin is completely removed.

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To determine the dilution and soluble hide errors, four different hide powders were used, samples of the different kinds that had been used in this laboratory from time to time.

1. Granular, color white, no smell, from E. & A.
2. Fine powder and wooly, color white, slight odor, Dr. F.
3. Fine powder and wooly but dusty, whitish blue, smells some, Dr. F.
4. Excellent wooly conditions, white and smells some, Vienna.

MOISTURE HELD BY THE POWDERS AIR DRY.

1. Per cent.	2. Per cent.	3. Per cent.	4. Per cent.
12.60	11.00	13.40	15.40

From this we see that even when the filter method is used there is a slight dilution, as the powder is used in the filter air dry.

MOISTURE HELD BY HIDE AFTER WASHING AND SQUEEZING.

	1.	2.	3.	4.
To absolute dryness per cent.	64.74	72 46	72.16	65.19
To air dry condition per cent.	59.79	68.53	67.67	58.96
Grams of water held by 6 grams hide absolutely dry when dampened and squeezed	10.79	12.07	12.02	10.87
Grams of water held by 6 grams air dry...	0.75	0.66	0.80	0.96

The dilution due to water from the squeezed hide can thus be readily corrected, while the slight dilution due to moisture in air-dry hide in the filter method can not be allowed for. However, the greater part of this dilution affects the first 30 cc., which are thrown away and as a point of error is trifling in the non-tannin filtrate used for the determination. It has been found that the amount of moisture held by the hide, if pressed the same, is uniform, and the determination of the water held by 3 grs. of wet hide will give that put in the tannin solution.

	1.	2.	3.	4.
Solids in grams.....	0.0550	0.1470	0.1585	0.0587
Ash in grams.....	0.0055	0.0110	0.01450	0.0057
Hide substance grams	0.0495	0.1360	0.1440	0.0530
Ammonia produced by 100 cc. in grams by hide.....	0.0061	0.0180	0.0220	0 0070
Ammonia per cent. in hide...	12.3	13.2	15.2	13.2
Ammonia in non-tannin filtrate 100 c., in grams.....	0.00072	0.00200	0.00188	0.00088
Ammonia in non-tannin filtrate then represents hide in 100 cc., grams	0.0058	0.0151	0.0123	0.0067
Per cent. of the hide in the non-tannin filtrate of that soluble on the first shaking on the same hide.....	11.8	11.1	8.5	12.6

I have endeavored to obtain some data of the soluble hide error in the following way: Gelatin by boiling with an alkaline solution of permanganate of potash, as in Wanklyn's method of water analysis, gives, according to him, 10 per cent. of ammonia. It is, I think, a fair conclusion that the soluble matter in the non-tannin filtrate will give proportionately the same amount of ammonia as that which is obtained in the first washing

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of the hide and which can be weighed. With this in view, I made the following determinations:

By shaking thirty minutes 10 grams of hide with 200 cc. of water and evaporating 100 cc. there was found in the 100 cc. evaporated, the results given in the above table.

To get this data the following procedure was observed:

Ten grams of hide were shaken with 200 cc. of water filtered through paper, and 100 cc. of the filtrate evaporated and weighed.

Two cc. was diluted with ammonia free water and the albuminoid ammonia determined; the washed hide was then used to determine the non-tannin, and 5 cc. of the non-tannin filtrate analyzed for albuminoid ammonia.

A duplication of this washing of the hide, etc., the same as above, when, instead of determining the non-tannins with the washed hide, it was used as in a determination of the non-tannins, using water instead of tan liquor, gave

	1.	2.	3.	4.
Solids in grams	0.0063	0.0212	0.0170	0.0075
Per cent. of this found in non-tannin filtrate	92.0	71.0	78.0	90.0

Generally speaking the most of the soluble hide to water is also soluble in the non-tannin filtrate. I would call special attention to the extent of the removal of this soluble hide by the preliminary washing. It seems to me that in this particular the shake process has a great advantage over the filter and that filter results will be higher in non-tannins; in fact, hide powders 2 and 3 could not be used in the filter with any degree of accuracy, because of the amount of soluble hide given by them, while it could not be used at all on account of its granular condition, yet the results from all, when corrected and before correction, are consistent.

We will now turn to the actual analysis:

	1.	2.	3.	4.
Grams extract in 500 cc. water	10.520	11.256	10.749	11.379
Grams total solids found	4.455	4.735	4.565	.30
Grams non-tannins found	1.735	1.825	1.720	1.880
Grams non-tannins corrected dilution	1.9284	2.0440	1.9264	2.0849
Grams hide correction	0.0290	0.0755	0.0615	0.0335
Grams non-tannins both corrections	1.8994	1.9685	1.8694	2.0404
Per cent. non-tannins without corrections	16.49	16.21	16.00	16.47
Per cent. non-tannins with dilution corrections	18.33	18.17	17.92	18.31
Per cent. non-tannins with both corrections	18.05	17.40	17.35	17.93
Per cent. solids	42.35	42.24	42.46	42.44
Per cent. tannins without corrections	25.86	26.03	26.46	25.97
Per cent. tannins with dilution corrections	24.02	24.07	24.54	24.1
Per cent. tannins with both corrections	24.30	24.84	25.11	24.51

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In comparing this method with the filter we have a greater dilution, but one which can be accurately measured. By shaking, we remove very largely the soluble hide. In the filter, the result depends upon the hide. Having shown that the hide that is soluble in water is also very nearly as soluble in the filtrate, that the tannins do not precipitate very much of this soluble hide during the course of the analysis, it is not to be presumed that the 30 cc. thrown away removed the soluble hide to anything near the extent that washing with 200 cc. of water does. Application of a permanganate and soda solution would give relatively the amount of hide in the filter filtrate, but I have not had the time as yet to apply it. Whatever empirical method is adopted by this Association as a standard will have to have its rules very strictly laid down and adhered to, and I believe that for accuracy, rapidity, and ease of working this method is the best. Further, I have no doubt that with well-defined rules of manipulation and correction, that not only can different operators get the same result with the same hide powder, but also with different hide powders and with hide powders which would make it impossible to do any concordant work with the filter.

"HEMLOCK REDS."

By J. N. Hurty.

Under this title I have an account to give of a few facts and of a few experiments; but the paper will contain very little that is conclusive. It is my hope that something herein will prove of value in some way.

My sample of "reds" was obtained from Mr. W. B. Taber, of Alpena, Mich. He informs me that the substance he sent "must be formed during the evaporation under reduced pressure, for the liquors are clear and free from sediment when they enter the pan. The precipitate appears when the evaporation has slightly advanced, and is at its maximum when the concentration is about one-half done. The reds are separated by subsidance." The sample I received weighed several pounds, and was in lumps about the size of walnuts down to very small pieces. The lumps were damp, but quite firm, and in places upon their surface red patches appeared. Fracture was uneven, the freshly exposed surfaces having a deep blue-black color. When cut with a knife the surfaces showed a metallic luster in places, and in other places a dark brown-red color. The odor was that of wet hemlock bark, and the taste, at first faintly sweet, was followed by a slight astringency and bitterness. The bitter was very transitory. The lumps parted with their moisture easily and quickly, and when dry were without difficulty reduced to a brown-red powder. In distilled water at the ordinary temperature 32.62 per cent. of matter was dissolved. The remainder was true reds mixed with a small amount of fiber. Of the matter dissolved 48.68 per cent. united with hide, which is equivalent to 15.88 per cent. of the original substance. This leather-making matter, being soluble, is most probably occluded tannin. In a 1 per cent. solution

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of hemlock extract 21.68 per cent. of matter from the reds was dissolved, a difference in favor of water of 10.94 per cent. In a 2 per cent. solution of hemlock extract 14.94 per cent. of the reds was soluble, a difference in favor of water of 17.68 per cent. These two experiments make it apparent, as was to be expected, that the reds grow less and less soluble in an extract solution as that solution is made stronger. The tanning substance taken up by hide from the water soluble matter in the reds was 15.88 per cent.; in a 1 per cent. solution of hemlock extract it was 8.44 per cent., and in a 2 per cent. solution of the extract it was 9.26 per cent. This increase of tannin in the 2 per cent. solution (although it dissolved less matter from the reds) would indicate that varying strengths of extract solutions will take up from the reds irregular quantities of tanning substances. Further experimentation might, however, show this conclusion to be an error. I have been told of instances in the actual process of tanning where reds which were abundant in the vat at the beginning of the process gradually disappeared, the supposition being that they eventually made leather, or at least entered into the hide and gave weight. My slight study of the problem furnishes no contradiction of this conclusion, but there are good reasons for believing that a copious deposit of reds on the hides retards the tanning process not a little. That reds in the tanning vat might in time—because of change in the liquor—dissolve, I can not deny, but my experiments so far do not corroborate the statement. The reds under examination contained —

	Per cent.
Ash	0.765
Matter soluble in petroleum ether	0.208
Matter soluble in acetone	52.290
Matter soluble in alcohol of 0.848 sp. gr. after petroleum ether	67.71

The color of the residues after treatment with alcohol and acetone differ materially. They both were red-brown, but that from acetone was very much the lightest.

No other papers being presented the report of the reporter was discussed.

Mr. Yocum did not think that a variation in the speed with which the shaking was carried on would influence the results.

Mr. Westenfelder considered this worthy of investigation, and Mr. Yocum agreed to experiment on this point and report at the next meeting.

Mr. Yocum suggested that all results during the ensuing year be figured to a dry basis.

Mr. Kepich stated it as his belief that results so figured would not be as valuable and more apt to give an erroneous impression. It was decided to leave this to the option of the members.

Mr. Westenfelder said that fermentation would increase the per cent. of tannins by destroying the non-tannins. He did not think that the tannis would be readily destroyed by fermentation.

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The advisability of increasing the quantity of liquor and hide powder used in an analysis and of adding all the hide powder at once was then discussed.

MR. YOCUM: I think that we should use 10 grams of hide powder and 150 cc. of liquor. The wet hide powder should be weighed after pressing and the water determined in about 3 grams by drying. A correction can then be made for the water retained.

MR. WESTENFELDER: I think this correction an important one.

Mr. Fiebing's results show the wide difference caused by this retained water.

Mr. Kerr moved that Mr. Yocum's recommendations be adopted.

The motion was carried.

MR. KRUG: I think the subject of the hide powder is a most important one. We should decide upon some limit for the soluble matter, and also determine which form of powder it is best to use.

MR. YOCUM: I think that we should reject any hide powder which gives more than 0.10 gram of residue when 10 grams are shaken for ten minutes with 200 cc. of water and 100 cc. of the filtrate evaporated to dryness.

MR. KEPICH: We ought to make the method of testing the hide powder conform to the official method. I would suggest that we shake the hide powder three times with water, using 200 cc. each time, and evaporate 100 cc. of the last filtrate. If the residue amounts to more than 0.01 gram the hide powder must be rejected.

MR. KRUG: I think Mr. Kepich's method of testing a good one, and move that it be adopted.

The motion was carried.

MR. WESTENFELDER: I move that the following paragraphs be inserted in the method:

"The hide powder must be kept in a dry place and must be tested once a month."

"The above method is applicable to extracts, barks, and all sweet liquors."

The recommendations of the reporter were then adopted.

The society prepared a letter asking for recognition by the Association of Official Agricultural Chemists, and the appointment of a reporter on tannin by said society.

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REFERENCES.

Tannin.

Snyder, H., Notes on Lowenthal's method. *Jour. Am. Chem. Soc.*, **15**, 560-562.

Procter, H. R., Qualitative determination of tannins. *Jour. Am. Chem. Soc.*, **16**, 247.

Procter, H. R., The technical tanning materials, especially gambier, analysis of. *Jour. Soc. Chem. Ind.*, XI., 329.

Wood, J. T., Fermentation in the leather industry. *Jour. Soc. Chem. Ind.*, XIII, **3**, 218.

Procter, H. R., Note on the estimation of tanning matter. *Jour. Soc. Chem. Ind.*, XIII, **5**, 494.

Canaigre as a substitute for barks. *U. S. Consular Reports*, 1894, **44**; *Jour. Soc. Chem. Ind.*, XIII, **6**, 650.

Trimble and Peacock, Canaigre tannin. *Am. Jour. Pharm.* XXIII, **4**, 161.

Trimble and Peacock, The preparation of oak tannin, with special reference to the use of acetone as a solvent. *Am. Jour. Pharm.* XIII, **9**, 435.

Hooper, David, Myrica Nagi Thun. *Am. Jour. Pharm.* XXIV, **5**, 209.

Manager, Ch. C., Myrica asplenifolia. *Am. Jour. Pharm.* 1894, **66**, 211; *Chem. Ztg.*, XVIII, **58**, 186.

Culley, John. The Tannin of Pumica granatun. *Am. Jour. Pharm.* XXIV, **6**, 280.

Thompson, Wm. B., Oak wood and bark. *Am. Jour. Pharm.*, XXIV, **6**, 293.

Trimble, Henry, Oak barks from India. *Am. Jour. Pharm.* XXIV, **6**, 299.

Hooper, David, Indian tanning materials. *Am. Jour. Pharm.* XXIV, **8**, 377.

Haenlein, F. H., Origin of acid fermentation in tanning liquors. *Dingl. polyt. Jour.*, 1894, **291**, 188-190.

Sadlon, C., The course of absorption in the tannin layers. *Dingl. polyt. Jour.*, 1893, **288**, 256.

Von Schroder, Practical extraction of myrobalans. *Dingl. polyt. Jour.*, 1894, **75**, 213; *Chem. Ztg.*, XVIII, **52**, 169.

Schroder and Bartel, Extraction of tanning materials. *Dingl. polyt. Jour.*, 1894, **291**; 259-263.

Fahrion, Dr. W., The theory of the formation of leather. *Chem. Ztg.*, XVII, **23**, 394.

Jean, F., Analysis of tannin extracts. *Chem. Ztg.*, XVII, **27**, 470.

Paessler, Dr. J., Does tannin tan? *Chem. Ztg.*, XVIII, **21**, 363.

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Folsing, Dr. A., Progress in the field and tanning substances. *Chem. Ztg.*, XVIII, **96**, 1770.

Eitner, W., The influence of light, heat, and fermentation on the composition of tanning substances. *Der Gerber*, **13**, 245.

Morpurgo, G., Estimation of tannin. *Der Gerber*, **18**, 288; *Ztschr. anal. Chem.*, **32**, 617.

Weiss, B., Criticism of the use of lead carbonate for estimating tannin. *Der Gerber*, **18**, 288.

Bartel, A., Purification of hide powder. *Deutsche Gerbertztg.*, **35**, No. 56.

Porcter, Solubilities of tannin. *Deutsch-Amerik. Apoth. Ztg.*, **10**, 276; *Ztschr. anal. Chem.*, **32**, 616.

Trimble, Henry. Examination of the tannin of chestnut bark. *Proc. Frank. Inst.*, **4**, 23.

Fluckiger, F. A., Notes on tannins. *Pharm, Post*, **27**, 233.

Fleury, G., The estimation of tannin. *Jour. de Phys. et de Chim.*. (5 ser.), **25**, 499; *Bull. Soc. Chim.*, Paris (3 ser.), **7**, 687.

Gawalosky, A., Estimation of tannic acid, gallic acid, and pectin. *Brestewski's Handworterbuch der Pharmacie.*

Production of gambier in India. *Pharm. J. Trans.* (1894), 1228, 54.

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FOREWORD

Prior to the publication of our JOURNAL almost all the experimental collaborative work of the leather chemists was published in the annual proceedings of the annual conventions of the Association of Official Agricultural Chemists. Some of these are difficult to obtain and a number of our members probably do not have access to files of this publication. More familiarity with some of this work apparently would have tended to lessen duplication of experimental work in a number of instances during

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recent years. At the last annual meeting it was suggested that such matters as would be of interest to us should be republished for the benefit of our members and the Editor was instructed to have this done in such a manner as he thought best. We have decided therefore to make up this number of the JOURNAL in this manner. All of the matter that we can find pertaining to the subject of tannin analysis which was published in these proceedings previous to the publication of our JOURNAL is therefore contained in this number.

REPORT ON TANNIN

By William H. Krug.

Bulletin No. 47 U. S. Dep't. of Agriculture. Proceedings of the Twelfth Annual Convention of the A. O. A. C. held at Wash., D. C., Sept. 5, 6 and 7, 1895.

In accordance with the instructions of the association, the reporter on tannin this year sent out a sample of extract and two samples of hide powder—No. 1, from Richards & Co., being granular, and No. 2, from Mr. Fiebing, being fibrous. These samples were accompanied by a circular letter giving an outline of the special work desired. There seems to have been a lack of interest, though, and several chemists on whom the reporter relied for extensive and valuable reports failed to send any data whatever. This must be deplored, as I believe that the work has arrived at a stage where some radical changes will be made, and where the utter uselessness of the hide powder method is proved.

In addition to the regular work done on the provisional method, as modified at the last meeting the following special work was requested from the analysts.

1. Total solids determination:

Method 1. Dry 5 grams of the extract at 100° until the residue ceases to lose weight.

Method 2. Dry 100 cc. of the diluted extract at 100° until the residue ceases to lose weight.

Method 3. Heat good porous pumice stone until all moisture has been driven off. After cooling, cut it into pieces (1) 1 cm. square and (2) smaller particles which pass through a sieve having six meshes to the inch. Cover the bottom of a flat platinum dish of proper size with the small particles, and on these place a layer of the larger pieces. Heat the dish and contents to redness for about fifteen minutes, cool, and weigh. By means of a small pipette with a small nozzle, distribute from a hand flask about 10 grams of the diluted extract evenly over the larger pieces. Dry at 100° until constant weight is obtained. This should be accomplished in a few hours.

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TABLE 1.—GENERAL TABLE OF RESULTS.

Analyst	Total Solids			Soluble solids	Tanning Substances					
					Method a		Method b		Method c.[1]	
	Method 1.	Method 2	Method 3		Hide powder 1	Hide powder 2	Hide powder 1	Hide powder 2	Hide powder 1	Hide powder 2
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
J. H. Yocum	43.33	43.55	43.38	42.15	—	—	16.21	16.78	16.80	17.06
G. A. Kerr	—	43.38	43.71	41.71	—	—	14.80	10.54	14.34	14.70
B. D. Westenfelder	44.52	44.24	43.47	43.19	—	—	17.29	17.34	17.20	17.40
J. L. Fiebing	41.70	41.70	41.65	38.10	15.70	15.70	15.30	15.30	17.10	17.10
W. H. Krug	43.11	42.71	45.00	42.35	15.73	16.02	14.98	14.65	15.87	16.41
J. S. Carman	43.52	42.68	—	40.87	—	—	—	—	—	—
F. L. Johnson	43.25	42.72	43.09	—	—	—	—	—	—	—
J. N. Hurty	42.67	42.98	—	41.60	—	—	13.58	16.08	16.54	16.54
Means	43.16	42.99	43.39	41.42	15.72	15.86	15.36	15.11	16.31	16.52
Difference between maximum and minimum	2.82	2.54	4.65	5.09	—	—	3.71	6.80	2.86	2.70

[1] Provisional method.

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2. Tannin estimation:

Make a series of determinations:

(a) Using the three portions of hide powder without intermediate filtration.

(b) Using the hide powder all at once.

The opinion of the various analysts on the best method of filtration was also desired, as well as any additional work which might be suggested during the course of the regular investigation.

Five chemists sent in full reports, while two others reported determinations of the solids.

Only three chemists sent in data on the hide powder. These showed that neither sample came within the requirements of the association.

Residue from 100 cc. of final filtrate, 10 grams hide powder washed three times with 200 cc. of distilled water.

Analyst	No. 1 Per cent	No. 2 Per cent.
J. H. Yocum[1]	0.1015	0.0428
Wm. H. Krug	0.0211	0.0288
G. A. Kerr	0.0450	0.0340
J. N. Hurty	0.0230	0.0170

[1] Mr. Yocum used only 9 grams of hide powder.

The separate reports contain much that is of interest, and I therefore give extracts from them.

Mr. Yocum characterized hide powder No. 1 as being one that without great care would give wrong results, as it contains much soluble matter. He also analyzed the extract with two other hide powders, the first being used dry, the second, an old sample, washed in the customary manner. The first gave 29.34 per cent. non-tannins (12.81 per cent. tanning substances), and as this hide powder contained 0.0800 gram soluble matter, which, when deducted from the residue, gives 25.22 per cent. non-tannins (16.93 per cent. tanning substances), it is quite evident that all this soluble matter must have practically passed into the final liquid. The second hide powder, about two years old, gave 27.96 to 28.02 per cent. non-tannins (14.16 per cent. tanning substances), which low result was no doubt due both to poor absorptive power and solution of soluble matter from the hide. Mr. Yocum found that on dissolving the extract in cold water more insoluble matter was left behind. Thus, by the usual method the insoluble matter or reds was 1.27 per cent. (42.15 per cent. soluble solids), while solution in cold water (17°) gave 2.15 per cent. (41.27 per cent. soluble solids). He examined the hide powders used in his work with the following results:

WEIGHT OF RESIDUES OBTAINED.

Kind of hide powder	9 grams of hide powder washed three times with 200 cc. of water; 100 cc. of final filtrate evaporated	30 grams of this (= 8 grams dry) shaken with another 200 cc. of water for 15 minutes, and 100 cc. evaporated	9 grams of hide powder washed once with 200 cc. of water and 100 cc. of filtrate evaporated
No. 1	0.1015	0.0040	0.2840
No. 2	0.0428	0.0060	0.1480
Laboratory	0.0197	0.0040	0.0800

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All these figures throw out the two hide powders sent. The following figures were obtained with the hide powder used in the laboratory:

	Per cent.	
Non-tannins by official method	25.92 = 16.23	tanning substances
Non-tannins, using all hide powder at once, shaken twenty minutes	25.89 = 16.26	" "
Non-tannins, using hide powder dry	29.34 = 12.81	" "

Mr. Yocum thinks that the solution is best filtered by passing 250 to 300 cc. through paper before taking the amount required for analysis, and entirely discarding that which passes through first.

Mr. Kerr, associate reporter on tannins, became thoroughly disgusted with hide powder during the work, and subsequently wrote me that he was using a new method suggested by Mr. Stüercke, of Chicago. This consisted of forcing the tannin liquor through a column of asbestos impregnated with mercuric oxide. In his final report he sends the following results on the official extract with this method:

RESULTS WITH MERCURIC OXIDE METHOD.

Dilution	Amount of reagent used	Soluble solids Per cent.	Insoluble matter (reds) Per cent.	Tanning substances Per cent.
5.093 grams, 1,000 cc...	2 grams HgO and 5 grams asbestos	41.80	1.90	23.20
20.36 grams, 1,000 cc...	"	41.74	1.53	22.79
"	2 grams HgO and 10 grams asbestos	41.74	1.53	23.34

Mr. Kerr wrote that in no case could either mercury or tannin be found in the final filtrate, and that he was therefore using this method altogether in his laboratory.

Mr. Westenfelder writes that he used both filter paper and asbestos fiber with filter pump, and found no appreciable difference in the results for total soluble matter, though the pumps filtered much more rapidly. He had considerable difficulty in filtering the non-tannin solution from the hide powder, and obtained the best results by filtering through the hide powder which had been shaken up with the liquid.

Mr. Fiebing finds it necessary to use the hide powder in three separate portions, and gives the following figures in proof: Official extract, per cent. non-tannins: (a) Using three portions of hide powder without intermediate filtration, 22.4 per cent.; (b) using hide powder all at once, 22.8 per cent.; (c) using hide powder in two portions with intermediate filtration, 21.7 per cent.; (d) using the hide powder in three portions with intermediate filtration, 21 per cent. Fresh hemlock liquor, non-tannins: (a) Four portions of hide powder with intermediate filtration, 1.95 per cent.; (b) three portions of hide powder with intermediate filtration, 2 per cent.; (c) three portions without intermediate filtration, 2.10 per cent. Leached hemlock bark, non-tannins: (a) Three portions of hide powder with intermediate filtration, 1.58 per cent.; (b) three portions of hide powder without intermediate filtration, 1.68 per cent.

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Discussion of Results.

On comparing this year's results with those of last year, one thing is immediately very evident, and that is that the discrepancies are greater than ever. The figures obtained by the various analysts for total solids agree fairly well with the exception of those reported by Mr. Fiebing. The column "Soluble solids" shows a great variation, and it seems to me that one source of the trouble we have experienced lies here. Mr. Yocum's work on the insoluble matter obtained by hot and cold solution, shows that variations in the temperature of the water used can cause considerable variation in the amount of soluble solids. I did some work on this point and obtained the following figures, which confirm those of Mr. Yocum:

(Per cent. Soluble Solids)

10 grams extract dissolved in cold water made up to 500 cc.	10 grams extract dissolved in water at 80° and made up to 500 cc. when cool.
40.46	42.46
40.42	42.23
40.42	—

Here is a difference of almost 2 per cent., which, when the extract is properly dissolved, will go to the credit of the hide powder. I do not mean to say by this that more care in the manner of dissolving the sample will insure better or more concordant results. I do not think that such results can be obtained with hide powder, and that we will sooner or later be forced to discard it. The differences between the results obtained by different analysts are too great to be ascribed to anything but the reagent itself. The manner of carrying out the method could not differ so radically among chemists as to account for these discrepancies. The results also indicate that there is no radical difference between the two hide powders, *i. e.*, excepting the results obtained by Mr. Kerr in using all the hide powder at once.

Shortly after the last meeting, Mr. Kerr wrote to various firms asking for samples of their best hide powder. He received a number of samples, which he analyzed. Unfortunately, I do not have the figures at hand, but his report showed the granular powder from Richards & Co. and the fibrous powder made by Mr. Fiebing to come within the requirements of the association. On the strength of this, these powders were used, and the subsequent results show the unreliability of hide powder in general. It is evidently impossible to obtain two samples of hide powder even approximately similar, and the differences between the residues from 100 cc. of the final washing of the powder shown in Table 2 indicate that this variation extends even to the small samples sent out. Such being the case, I do not see how we can place any reliance on the reagent or results obtained by it. I think the work of the last two years shows this very plainly, and indicates that the realization of a good, reliable method lies in another direction. I do not at this time venture to say where we

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shall turn for a new method, although I think that the experimental work which I will now discuss seems to point a way to get out of the dilemma. As I stated above, Mr. Kerr, during the progress of our joint work, sent me a description of the mercuric-oxide method as he was using it, and also an apparatus already charged and ready for use. I made a number of estimations by this method, but the results varied so much that I do not consider them worth reporting. Subsequent developments showed that my failure was mainly due to the variety of asbestos I used, though at the time I ascribed it to other causes, such as unequal packing and distribution of HgO, imperfect contact, etc. This work, however, suggested another line of investigation to me, which I will discuss briefly. Failing to get good results by percolation, I turned to find another method of using mercuric oxide, and finally decided to apply it exactly as the hide powder is now used. I subsequently extended the work to several other oxides. It was evident at the beginning that considerably more time would be consumed in absorbing the tannin in this manner, and a number of experiments were made to determine the time limit. In all cases where upon filtration after shaking a certain length of time it was found that combination was incomplete, the mixture was allowed to stand until this was accomplished. It was thus found that with mercuric and magnesium oxides it was best to shake about four hours and then let the mixture stand over night, when it would be ready for filtration. With lead oxide the process required two days, after being shaken four hours, and the mixtures with zinc oxide stood a week before the tannin was totally absorbed.

The last two oxides were therefore rejected as requiring too much time, although the analyses made with them are given for comparison. The diluted extract gave in 25 cc. as a mean of three determinations 0.0113 gram ash, containing 0.0006 gram MgO. The ash determinations were made as a check on the amount of oxide dissolved during analysis.

EXPERIMENTS WITH ZnO.

Method	ZnO used Grams	Diluted extract used cc.	Filtrate evaporated cc.	Weight of residue Gram	Tannin in extract Per cent.	Ash in residue Gram	ZnO in ash Gram
Shaken 4 hours, stood over night	2	75	25	0.1095	20.45	0.0125	0.0008
Shaken 4 hours, stood over night	2	75	25	0.1174	18.87	0.0147	0.0016
Shaken 4 hours, stood 1 week	2	75	25	0.1049	21.37	0.0095	—
Shaken 4 hours, stood 1 week	2	75	25	0.1029	21.97	0.0103	0.0030
Shaken 4 hours, stood 1 week	2	75	25	0.1029	21.97	0.0100	0.0020

The first two filtrates gave a faint reaction for tannin, but were run through so as to compare the results with those obtained with other oxides,

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during the same length of time. The last three gave no test for tannin, and agree fairly well. They are low, compared with lead and mercury oxides, and agree better with those obtained with magnesium oxide. The amount of zinc oxide dissolved is too small to affect the accuracy of the analysis, and the only objection to the use of this oxide is the slow action, which makes it impracticable in a laboratory when rapid work is desired.

EXPERIMENTS WITH LEAD OXIDE, PbO.

Method	PbO used Grams	Diluted extract used cc.	Filtrate evaporated cc.	Weight of residue Gram	Tannin in extract Per cent.	Weight of ash from residue Gram	Ash contained PbO Gram
Shaken 3½ hours, stood 2 days	4	75	25	0.0738	27.59	0.0111	0
Shaken 3½ hours, stood 2 days	4	75	25	0.0754	27.27	0.0092	0
Shaken 3½ hours, stood 2 days	4	75	25	0.0706	28.23	0.0105	0

None of these gave a reaction for tannin. The results were higher than with any oxide used. The objection to lead oxide is the length of time required for complete absorption.

Table 2 shows that a considerable amount of the oxide is dissolved and passes into the filtrate, increasing the weight of the residue and correspondingly lowering the tannins. This error does not seem to be constant, so that no correction can be made for it.

The analyses in Table 3 show that even though the conditions may be varied fairly concordant results can be obtained with HgO as long as care is taken to insure the complete absorption of the tannin before filtering. The end of the reaction may be easily observed with all the oxides used, and especially so with HgO, since, when it is reached, the oxide no longer sinks to the bottom after shaking, but the whole mass partially gelatinizes and becomes a dirty brown in color. A clear filtrate, free from tannin and mercury, can then be easily obtained. The results in the ash column indicate that a certain amount of the ash present in the extract is held back, but this error is quite constant and so small as to have little influence on the result. Although the time required for the analysis of a tanning liquor by this method is somewhat longer than with hide powder, still the uniform results obtained more than compensate for this, and at the most an analysis will not take more than two days. A number of analyses can be made at a time by adapting a shaker, so as to hold several 100 cc. sugar flasks, which are of a convenient size for this work.

After I had commenced this work just reviewed, Mr. Kerr wrote me that he had discovered that the asbestos which he had been using absorbed tannin completely. He sent a sample, which I tested and found to be a true absorbent, just as he had stated. A quantity which I subsequently ordered from Richards & Co., in Chicago, also possesses this remarkable property, which I have been unable to explain, except by the presence of an excess of some oxide, such as MgO, which combines with the tannin.

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TABLE 2.—EXPERIMENTS WITH MAGNESIUM OXIDE.

Method	MgO used Grams	Diluted extract used cc.	Filtrate evaporated cc.	Weight of residue Gram	Tannin in extract Per cent.	Weight of ash in residue Gram	MgO in ash Gram
Shaken 2½ hours, stood over night	2	75	25	0.1134	19.67	0.0209	0.0055
Shaken 2½ hours, stood over night	2	75	25	0.1028	21.79	0.0195	0.0042
Shaken 2½ hours, stood over night	2	75	25	0.1230	17.75	0.0232	0.0052
Shaken 2½ hours, stood over night	2	75	25	0.1246	17.43	0.0247	0.0058
Stood 24 hours, occasional shaking	2	75	50	0.2063	21.72	0.0252	0.0074
Stood 24 hours, occasional shaking	2	75	50	0.2061	21.74	0.0244	0.0076
Stood 24 hours, occasional shaking	2	75	25	0.1157	19.21	0.0213	0.0044
Stood 24 hours, occasional shaking	2	75	25	0.1114	20.07	0.0205	0.0038
Stood 48 hours, occasional shaking	2	75	50	0.1941	22.94	0.0326	0.0064
Stood 48 hours, occasional shaking	2	75	50	0.1959	22.76	0.0339	0.0070
Shaken 3½ hours, stood over night	2	75	50	0.2165	20.70	0.0349	0.0102
Shaken 3½ hours, stood over night	2	75	50	0.2191	20.44	0.0355	0.0111
Shaken 3½ hours, stood over night	2	75	50	0.2179	20.56	0.0359	0.0115

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TABLE 3.—EXPERIMENTS WITH MERCURIC OXIDE (YELLOW).

Method	HgO used Grams	Diluted extract used cc.	Filtrate evaporated cc.	Weight of residue Gram.	Tannins in extract Per cent.	Ash in residue Gram	HgO in ash Gram
Stood 48 hours, occasional shaking	4	75	25	0.0833	25.69	0.0070	0
Stood 48 hours, occasional shaking	4	75	25	0.0829	25.77	0.0077	0
Stood 48 hours, occasional shaking	4	75	25	0.0829	25.77	0.0071	0
Shaken 1½ hours, stood over night	4	75	25	0.0842	25.51	—	—
Shaken 2 hours, stood over night	4	75	25	0.0867	25.01	—	—
Shaken 3½ hours, stood over night	4	75	25	0.0863	25.09	0.0081	0
Shaken 3½ hours, stood over night	4	75	25	0.0860	25.15	0.0080	0
Shaken 4 hours, stood over night	4	75	25	0.0839	25.57	0.0084	0
Shaken 4 hours, stood over night	4	75	25	0.0849	25.37	0.0065	0
Shaken 4 hours, stood over night	4	75	20	0.0638	26.41	0.0065	0
Shaken 4 hours, stood over night	4	75	20	0.0692	25.05	0.0103	0
Shaken 4 hours, stood over night	4	75	20	0.0682	25.29	0.0094	0
Shaken 4 hours, stood over night	4	75	25	0.0863	25.09	0.0083	0
Shaken 4 hours, stood over night	4	75	25	0.0849	25.37	0.0097	0
Shaken 4 hours, stood over night	4	75	25	0.0842	25.51	0.0084	0

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It was too late to do much work on this, and I was only able to make a few analyses, of which I report the last two, since they agree very well. Each analysis required 45 grams asbestos wool in four portions of 10 grams each and one portion of 5 grams, when the tannin was found to be absorbed, the residual liquor being only slightly colored and giving no reaction with ferric chloride. The two analyses gave 18.66 and 18.23 per cent. tanning substances, respectively, results which are somewhat higher than those obtained with hide powder and lower than those given by mercuric oxide.

This difference in results suggests another difficulty which confronts us. If the asbestos absorbs nothing but tannin, then mercuric oxide must combine with other substances which are not tannins, and we naturally ask whether these non-tannins are also absorbed by the hide in the process of leather making, and should be included in the valuation of an extract. These points need further investigation, and I would suggest that the work of the next year be concentrated on them, with the view of solving them as nearly as possible.

The president called for papers relating to the subject, and for the discussion of the report.

MR. GOSS: I have never done any work on tannin, but it seems to me that the hide powder method should certainly be well considered before being discarded. While it is true that the method may give poor results for the year, it is likewise true that we have the same variations in the substances we are trying to tan.

MR. KRUG: German chemists have come to the conclusion that when their results are off, it is the fault of the powder. I don't mean to drop hide powder, but I think another method should be tested. The hide powder gives most variable results. A difference of 7 per cent. can not be ascribed to differences in manipulation of the chemist, because the directions are strict and he ought to get within 0.5 of 1 per cent. A difference of 7 per cent. can not be accounted for otherwise except by the fault of the powder.

MR. MITCHELL: The tannin chemists have called us to account for determining tannic acid rather than the tanning power of the extract, and we have come to use the hide powder method as one giving approximately the results obtained. I think we have two things to determine, one the variations of the bark and the other of the substances to be tanned.

MR. KRUG: I would say concerning the official extract that we use, that if any chemist should report to the firm that is using it that it had only 17 per cent. of tanning substance the firm would call him to account for it. They know it has more than that. Two chemists reporting, one 10 per cent. and the other 17 per cent., would be called to account.

MR. MITCHELL: I think on hemlock bark the hide powder has had its best results and obtained its greatest hold.

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Mr. Goss called attention to a method in which permanganate of potash is used.

Mr. Krug remarked that the substances which tan leather are really not all tannic acid. He said there were other substances which entered into the composition of leather which are not tannic acid, and must be taken into consideration.

Mr. Goss said that all general methods were along the same line as the hide powder method.

AMENDED AND ADOPTED REPORT OF THE COMMITTEE ON RECOMMENDATIONS IN RELATION TO METHODS FOR THE ANALYSIS OF TANNING MATERIALS.

Bulletin No. 49 U. S. Dept. Agric.

(1) *Preparation of sample.*

Barks, woods, leaves, and similar tanning materials should be ground to such a degree of fineness that they can be thoroughly extracted.

Extracts must be heated to 50° C., well shaken, and allowed to cool slowly to room temperature.

(2) *Quantity of tanning material.*

In the case of barks, woods, leaves, etc., use such an amount of the material as to give about one gram of total solids per 100 cc. of solution, and extract in a Sohxlet or similar apparatus. In the case of extracts, weigh 20 grams dilute with water at 80°, cool slowly to 20°, and make up to a liter.

(3) *Determination of moisture.*

Dry 5 grams of the sample in a flat-bottomed dish at the temperature of boiling water until the weight becomes constant.

(4) *Determination of total solids.*

Shake the solution and without filtering immediately measure out 100 cc. with a pipette. Care must be taken to keep the solution at 20°. Evaporate in a weighed dish and dry to constant weight at the temperature of boiling water. The dishes in which the drying is conducted should be covered while they are in the oven in order to prevent loss.

(5) *Determination of soluble solids.*

Filter about 125 cc. of the solution (at 20°) through a double-folded filter (S. & S. No. 590, 25 cm.), returning the filtrate through the filter twice. Evaporate 100 cc. as before.

(6) *Determination of tanning substances.*

Prepare 20 grams of hide powder by shaking for five minutes with 250 cc. of water and straining through linen. Repeat the operation three times. Finally remove as much water as possible by squeezing in a press. Transfer the pressed hide powder to a covered dish and weigh. Dry to constant weight, at 100°, a portion approximately equal to one-fourth of

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the whole. To 200 cc. of the original unfiltered solution (at 20°), add the remainder of the hide powder, and shake for ten minutes. Add 5 grams of barium sulphate free from soluble salts and shake again for one minute. Filter immediately through a folded filter (S. & S. No. 590, 15 cm.), returning the first 25 cc. Evaporate 100 cc. as before. The weight of the residue must be corrected for the dilution caused by the water contained in the hide powder. The shaking must be done in some form of mechanical shaker. The simple machine used by druggists, and known as the milk shake, is recommended.

(7) *Testing the hide powder.*

(*a*) Shake 10 grams of the hide powder with 200 cc. of water for five minutes; filter through muslin or linen; squeeze out thoroughly by hand; collect the hide powder, and repeat the operation twice with the same quantity of water. Pass the last filtrate through paper until a perfectly clear liquid is obtained. Evaporate 100 cc. of the final filtrate in a weighed dish; dry at 100° until the weight is constant. If the residue amount to more than 10 milligrams the sample should be rejected. The hide powder must be kept in a dry place and tested once a month.

(*b*) Prepare a solution of pure gallotannic acid by dissolving 5 grams in 1 liter of water. Determine the total solids by evaporating 100 cc. of this solution and drying to constant weight. Treat 200 cc. of the solution with hide powder exactly as described in paragraph 6. The hide powder must absorb at least 95 per cent. of the total solids present. The gallotannic acid used must be completely soluble in water, alcohol, acetone, and acetic ether, and should contain not more than 1 per cent. of substances not removed by digesting with excess of yellow murcuric oxide on the steam bath for two hours.

(8) *Testing the non-tannic filtrate.*

(*a*) For tannin: Test a small portion of the clear non-tannin filtrate with a few drops of a 10 per cent. solution of gelatine (Nelson's). A cloudiness indicates the presence of tannin, in which case the determination must be repeated, using 25 grams of hide powder instead of 20 grams.

(*b*) For soluble hide: To a small portion of the clear non-tannin filtrate add a few drops of the original solution, previously filtered to remove reds. A cloudiness indicates the presence of soluble hide due to incomplete washing of the hide powder. In this case repeat the determination with perfectly washed hide powder.

REPORT ON TANNINS

By John H. Yocum, Associate Referee.

Bulletin No. 51, U. S. Dep't. of Agriculture. Proceedings of the Fourteenth Annual Convention of the A. O. A. C. held at Wash., D. C., October 26, 27 and 28, 1897.

Mr. Westenfelder, the referee for this year, sent out samples of tanning extract to various members of the association. These samples

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were accompanied by hide powder and a circular letter outlining the method to be pursued. Unfortunately, Mr. Westenfelder found he could not attend the meeting and turned the matter over to me as assistant referee to make the report, etc. Results were returned by five operators and are of a very satisfactory nature. Owing to a misunderstanding, last year's referee did not present a report. I made request to him for the data then collected that they might be embodied in this report, but have not received them.

The method outlined in the circular letter is as follows:

(1) Weigh about 20 grams of the sample; wash into flask with hot water, add cold water nearly to mark, cool, and make up to 1,000 cc.; shake thoroughly.

(2) Immediately measure out 100 cc. into a weighed dish and evaporate and dry to constant weight at temperature of boiling water. Result: Total solids.

(3) Filter about 125 cc. of solution through a doubled folded filter (S. & S. No. 590, 25 cm.), returning filtrate through filter twice. Evaporate and dry as before. Result: Soluble solids.

(4) Shake 20 grams hide powder with 250 cc. of water for five minutes; strain through linen. Repeat operation three times. Finally remove as much water as possible by squeezing the material in a press. Transfer the pressed hide powder to a covered dish and weigh. Weigh off a portion approximately equal to one-fourth of the whole and dry to constant weight. To 200 cc. of original solution, add the remainder of the washed hide powder, and shake for ten minutes; add 5 grams of $BaSO_4$ free from soluble salts and shake for one minute; filter immediately through a folded filter (S. & S. No. 590, 15 cm.), returning the first 25 cc. Filtrate must be absolutely clear; if not, repeat filtration till so. Evaporate 100 cc. and dry as before. The weight of residue must be corrected for the dilution caused by the water contained in the hide powder. The shaking must be done in some form of mechanical shaker. The machine used by druggists and known as the "milk shaker" is recommended. Result: Non-tannins.

(5) Shake 10 grams of hide powder with 200 cc. of water for five minutes; filter through linen; squeeze out thoroughly by hand; collect hide powder and repeat operation twice with the same quantity of water. Pass the last filtrate through paper until a perfectly clear liquid is obtained. Evaporate 100 cc. and dry as before. Residue should not amount to more than 10 Mg. The above is test for quality of the hide powder.

(6) Test a small portion of the non-tannin filtrate with a few drops of a ten per cent. solution of gelatin (Nelson's). Solution must remain unaltered (not the slightest turbidity).

(7) Test for soluble hide: Use a filtered solution (original) of the tanning material instead of the gelatin solution. There must be no turbidity.

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(6a) If the above test shows the presence of tannin, repeat whole operation with 25 grams of hide powder.

(7a) If above test shows the presence of soluble hide, repeat whole operation with a perfectly washed hide powder.

All dryings must be done at the temperature of boiling water, *viz.*, 97° to 99° C.

Dishes should be covered during drying and cooled in desiccators.

One hundred cubic centimeters of solution should be taken in all cases for evaporating and drying.

Dry 5 grams of sample in flat-bottom dish to constant weight for moisture.

The results reported are shown in the table. The maximum difference in total solids is 1.63 per cent.; in soluble solids, 1.80 per cent.; in non-tannins, 0.95 per cent.

Heretofore the major differences have been in the non-tannins, and the concordance in this particular in these results is very encouraging.

The soluble hide in the hide powder is reported as follows:

	Gram
Westenfelder	0.0050
Carr	0.0030
Haley	0.0010
Krug	0.0088
Yocum	0.0030

TABLE OF RESULTS.

Operator	Water Per cent.	Total Solids Per cent.	Soluble Solids Per cent.	Non-tannins Per cent.	Tannins Per cent.	Reds Per cent.
Westenfelder	57.74	42.26	41.02	16.52	24.50	1.24
Carr	59.21	40.83	39.22	16.96	22.76	1.61
Haley	58.69	41.31	40.63	16.68	23.95	0.68
Krug	58.99	41.01	40.32	16.95	23.37	0.69
Yocum	58.21	42.15	39.86	17.47	22.39	2.34
Mean	58.57	41.51	40.21	16.92	23.39	1.30
Maximum difference from mean	0.83	0.75	0.99	0.55	1.21	1.04

Mr. Westenfelder reports that 10 grams of hide powder gave less than 5 mg. of soluble material under conditions of testing hide. He obtained 19.18 per cent. non-tannins by shaking 200 cc. of the extract solution with 10 grams of dry unwashed hide powder.

Mr. Carr made report of 19.18 per cent. of non-tannins originally but later found upon going over his results an error in them, and reports 16.96 per cent. non-tannins as the correct result.

He dried the materials in vacuo at 100° C., which no doubt makes his results on solids a trifle lower than the others.

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Mr. Haley obtained 15.75 per cent. of non-tannins with the use of 50 grams wet-pressed official hide powder (equivalent to 10½ grams dry); 15.85 per cent. with 50 grams wet-pressed Vienna hide powder (equivalent to 12 grams dry), and 16.24 per cent. with 50 grams wet-pressed hide powder of his own make (equivalent to 11½ grams dry).

Mr. Krug obtained 16.24 per cent. non-tannins by the use of an unofficial hide powder that gave 0.0065 gram of soluble material.

I obtained 17.76 per cent. non-tannins from an unofficial hide powder.

These results show that, in the hands of operators accustomed to the work, the non-tannins can be obtained in better accord than can the results from simple drying of viscous solutions, such as the extract itself is.

It is generally recognized that the tannin determination is not one of a single substance, but rather of a group having much the same characteristics, and that besides the chemical union of tannin and hide there also occurs an occlusion by the hide of the other soluble materials in the extract. This precludes the possibility of obtaining anything like the exact concordance that is obtained by purely chemical methods.

The non-tannins, obtained by the various operators using the official and other hide powders on the official extract, show the variations possible with hide powders, answering their individual requirements, and emphasizes the necessity of some standard in this respect.

The differences in the results obtained on water and total solids are due to the same general causes that occasion differing results in the drying of other organic solids, and can be regulated to a great extent by uniformity of time and temperature of drying.

Because of the oxidation and decomposition undergone by organic matter when dried in the air it is impossible to obtain final results that represent the true percentage of water, yet most chemists making tannin determinations have not the facilities for drying in hydrogen or in vacuo, and it is as yet an open question if such treatment would prevent decomposition in tanning solutions; consequently it does not seem proper to suggest changes in this direction.

By specifying the length of time, temperature, and size of dish a better agreement may be obtained next year.

The soluble solids are influenced by the temperature of the solution when filtered. Inasmuch as the temperature of the laboratory seldom varies outside of the limits of 16° to 20° C., this has little influence. The filter paper causes differences, but S. & S. No. 590, 15 cm. seems to give results of a satisfactory nature.

There seems to be more cause for difference in the temperature of the solution at the time the extract is dissolved than from either of the above causes. A solution made by dissolving 20 grams of extract in 1,000 cc. of water at 16° C. stood four hours, and filtered through doubled

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folded 15 cm. S. & S. No. 590 paper gave 39.09 per cent. of soluble solids. The same solution standing eighteen hours gave 39.24 per cent. soluble solids. Evidently the reds that are first thrown down by contact with cold water are to a limited extent redissolved on standing. By dissolving the extract at 80° C. and letting stand four hours 40.05 per cent. soluble solids were obtained, and by letting stand eighteen hours 40.07 per cent. By dissolving at 25° C. and letting stand four hours 39.75 per cent. soluble solids were obtained, and by letting stand eighteen hours 39.62 per cent. By filtering with kaolin the solution made at 16° C. gave 37.54 per cent., that made at 25° C. gave 37.65 per cent., and that made at 80° gave 38.55 per cent. soluble solids. The ton-tannins were not influenced by any of the methods of dissolving, nor were they less from the kaolin filtrates.

Though the results upon non-tannins from this year's work are in fair accord, the variations due to the use of other than the official hide powder are wide. The lowest result is from Mr. Haley—15.75 per cent.—and the highest, my own—17.76 per cent.

The value of a standard hide powder or a means of knowing the efficiency of a given hide powder, is great. Six hide powders were tested according to the two tests given in last year's published method (Bull. 49, p. 118), the soluble-hide test and the gallo-tannin test.

Results of the year's work are given in the following tables:

TABLE I—ANALYSES OF HIDE POWDERS.

Sample	Moisture	Fat.	Ash.	Al_2O_3 and Fe_2O_3	CaO	MgO
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
No. 1	13.00	—	0.50	—	—	—
No. 2	12.40	0.49	2.66	0.25	2.61	0.04
No. 3	13.00	0.39	0.45	0.10	0.19	0.02
No. 4	12.30	1.07	0.17	0.08	0.07	0.01
No. 5	14.00	0.94	0.48	0.10	0.11	0.01
No. 6	12.00	0.65	0.73	0.15	0.18	0.02

TABLE 2.—COMPARISON OF WASHING TESTS ON VARIOUS HIDE POWDERS.

Sample	Quantity of air-dry hide Grams	100 cc. first washing Grams	100 cc. second washing Grams	100 cc. third washing Grams	100 cc. fourth washing Grams	Hide removed by four washings Per cent.
No. 1	20	0.0634	0.0134	0.0093	0.0076	1.31
No. 2	20	0.1719	0.0375	0.0165	0.0105	3.42
No. 3	20	0.2192	0.0525	0.0196	0.0096	4.32
No. 4	20	0.0720	0.0172	0.0154	0.0049	1.56
No. 5	20	0.2256	0.0415	0.0098	0.0058	4.10
No. 6	20	0.1172	0.0254	0.0110	0.0073	2.27

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TABLE 3.—COMPARISON OF GALLOTANNIN TEST ON VARIOUS HIDE POWDERS.

Sample	Weight of air-dry hide Grams	Weight of wet hide Grams	Dry hide in wet hide Per cent.	Weight of dry hide Grams	Dilution correction	Weight of the non-tannins Grams	Corrected non-tannins Per cent.	Tannin absorbed Per cent.
No. 1	20	27.70	44.40	12.30	1.077	0.0069	1.38	98.62
No. 2	20	33.70	27.00	9.10	1.123	0.0320	6.42	93.58
No. 3	20	37.10	28.00	10.39	1.134	0.0247	4.96	95.04
No. 4	20	32.20	35.00	11.27	1.105	0.0120	2.41	97.59
No. 5	20	37.40	31.50	11.78	1.128	0.0157	3.13	96.87
No. 6	20	47.30	22.90	10.83	1.182	0.0468	9.40	90.60

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In Table 1 is given the analysis of these hide powders, and Table 2 the result of washing according to the method; in Table 3 the results of the gallo-tannin tests.

Hide No. 2 would be judged poorly prepared from its high ash, and is outside the limits designated by the method for soluble hide. Hide powders Nos. 2 and 6 are outside the limits designated by the gallo-tannin test.

Hide No. 1 is this year's official hide powder. I did not have enough of it to carry on the full comparison. This left Nos. 3, 4, and 5 as satisfactory hide powders. These powders were used to make comparative determinations on an extract with the following result:

Sample	Non-tannins Per cent.
No. 2	18.82
No. 3	15.70
No. 4	14.72
No. 5	14.45
No. 6	18.58

Nos. 3, 4, and 5, which have satisfied the requirements, give fairly concordant results on the extract.

A further test was made by shaking for ten minutes 5 grams of air-dry hide powder with 200 cc. of water, containing 5.48 grams of gallo-tannin.

GALLOTANNIN PER GRAM OF HIDE POWDER.

Sample	Gram
No. 2, hide powder removed	0.0943
No. 3, " " "	0.2393
No. 4, " " "	0.3632
No. 5, " " "	0.6230
No. 6, " " "	0.1448

These hide powders, when completely tanned, do not show any great difference in the amount of tannin absorbed; hence it is a condition in the preparation of the hide powder that gives the more rapid absorptiveness.

These tests when applied to hide powders enable the chemist to keep a fair check on various makes of powder, and assure himself of the uniformity of a given maker's product, but more satisfactory would be the acceptance of some maker's product as a standard.

Your referee would suggest that some minor details of the method be changed and that the hide powder tests be made to conform with the method relative to washing the hide powder. With this in view, I would recommend (Bull. 49, p. 118) the following as the coming year's method:

RECOMMENDED TANNIN METHOD.

1. PREPARATION OF SAMPLE.

Barks, woods, leaves, dry extracts, and similar tanning materials should be ground to such a degree of fineness that they can be thoroughly

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extracted. Fluid extracts must be heated to 50° C., well shaken, and allowed to cool to room temperature.

2. Quantity of Material.

In the case of barks and materials requiring extraction, use such amount of material as will give about 1 gram of solids per 100 cc. of solution. In the case of extracts, weigh 20 grams, dissolve in 900 cc. water at 80° C., let stand for twelve hours, and make up extract to 1,000 cc. with water.

3. Moisture.

Dry 3 grams of the sample, if it be an extract, in a flat bottomed dish not less than 2½ inches in diameter to constant weight; if bark, etc., dry 10 grams.

4. Total Solids.

Shake the solution, and without filtering immediately measure out 100 cc. with a pipette, evaporate in a weighed dish, and dry to constant weight, at the temperature of boiling water. Dishes should be flat bottomed, and not less than 2½ inches in diameter.

5. Soluble Solids.

Filter about 125 cc. of the solution through a double-folded filter (S. & S., No. 590, 15 cm.), returning all the filtrate through once. To prevent evaporation, funnels should be inserted in small necked flasks and covered with watch glasses during the filtration. To determine total solids, evaporate 100 cc. of filtrate to dryness.

6. Non-tannins.

Prepare 20 grams of hide powder by shaking for five minutes with 250 cc. of water and straining through linen. Squeeze the magma thoroughly by hand, repeat this operation three times, finally remove as much water as possible by means of a press, weigh the pressed hide and take approximately one-fourth of it for moisture determination. Weigh this fourth carefully and dry to constant weight. Weigh the remaining three-fourths carefully and add them to 200 cc. of the original solution; shake ten minutes, and squeeze the tanned hide through linen. Collect this filtrate, add 5 grams of kaolin free from soluble salts, stir well and filter through folded filter (S. & S. No. 590, 15 cm.), returning the first 25 cc. Evaporate 100 cc. of the clear filtrate. The weight of this residue must be corrected for the dilution caused by the water contained in the pressed hide powder. The shaking must be done in some form of mechanical shaker. The simple machine used by druggists, and known as the milk shake, is recommended.

7. Tannins.

The amount of these is shown by the difference between the soluble solids and the corrected non-tannins.

8. Testing Hide Powder.

A. Shake 10 grams of hide powder with 250 cc. of water for five minutes, strain through linen, squeeze the magma thoroughly by hand;

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repeat this operation three times, pass the last filtrate through paper (S. & S., No. 590, 15 cm.) till clear, evaporate 100 cc., and dry. If this residue amount to more than 10 mg., the hide must be rejected.

B. Prepare a solution of pure gallo-tannin by dissolving 5 grams in 1,000 cc. of water. Determine the total solids by evaporating 100 cc. of this solution and drying to constant weight. Treat 200 cc. of the solution with hide powder exactly as described in paragraph 6. The hide powder must absorb at least 95 per cent. of the total solids present. The gallo-tannin used must be completely soluble in water, alcohol, acetone, and acetic ether, and should not contain more than 1 per cent. of substances not removed by digesting with excess of yellow mercuric oxide on steam bath for two hours.

9. TESTING NON-TANNIN FILTRATE.

A. For tannin.—Test a small portion of the clear non-tannin filtrate with a few drops of a 1 per cent. solution of Nelson's gelatin. A cloudiness indicates the presence of tannin, in which case repeat the process described under 6, using 25 instead of 20 grams of hide powder.

B. For soluble hide.—To a small portion of the clear non-tannin filtrate add a few drops of the filtered tannin solution. A cloudiness indicates the presence of soluble hide, in which case repeat the process described under 6, giving the hide powder a more thorough washing.

The temperature of solutions when measured or filtered should not be below 16° C. or above 20° C. All drying should be made in flat-bottomed dishes of at least 2½ inches diameter. S. & S., No. 590, 15 cm. filter paper should be used on all filtrations.

PREPARATION OF TANNING EXTRACTS FOR ANALYSIS

By Robert H. Forbes.

While perfecting a method for the determination of tanning materials in canaigre, the writer was led to make some observations on the method of extraction, which are of general application.

Much of the inaccuracy of the hide powder method, as applied to barks, woods, leaves, etc., is without doubt due to the manner of extraction laid down in the official methods. It is there advised that the ground material be digested over night at 80° with 500 cc. of water. Under these circumstances a loss of tanning materials takes place, which is due to their slow recombination with the cellulose, starch (if present), and albuminoids of the material under examination.

Since the time of digestion, being "overnight," is not constant, and since the condition and amount of cellulose, starch, and albuminoids are variable, the amount of error due to their slow recombination is very irregular. In order to avoid this recombination, it is evidently necessary to devise a method by which the dissolved tannins shall be removed as promptly as possible from the extracted residue.

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Extraction by percolation is a simple and nearly perfect way to accomplish this, and it is noticed on page 118 of the Proceedings of the Association for 1896 that it is recommended by the committee to extract barks, woods, leaves, etc., in a Sohxlet or similar apparatus, no details, however, as to temperature and time of extraction being given.

These considerations are of importance, inasmuch as certain materials containing difficultly soluble matters, such as hemlock bark, can not be completely extracted at lower temperatures, while canaigre, which contains starch, can not be percolated at above 50° to 55° C., because of the solution of starch with its consequent inaccuracies.

The following work was carried through with oak, hemlock and canaigre in order:

(1) To establish the fact of error due to recombination of tannings with exhausted residues when these are left in contact with the water extract.

(2) To test the percolation method of extraction and note the modifications of temperature needful with different materials.

The reabsorption of tanning materials was established in the following way: A Sohxlet extractor was fitted with a 100 mesh brass wire gauze disk pushed nearly to the bottom of the tube, and a mat of woolly asbestos (previously extracted with HCl) deposited on the gauze and covered with fine asbestos.

The extractor was then placed in a sheet metal tank of suitable dimensions and 8 to 10 inches deep, the bottom being perforated with holes which received the rubber stoppers, through which the lower ends of the Sohxlets project. The tank was then filled with water of the desired temperature and kept at that temperature by a flame below. A weighed amount of finely ground material, 5 to 10 to 20 grams, was floated into the extractor, which was then fitted at the top with a tightly fitting rubber stopper carrying a 250 to 500 cc. drop funnel. The funnel was filled with water and the rapidity of the percolation controlled by the stopcock.

The percolates (500 cc.) were divided into two equal portions. One portion was examined as it stood for tannins and non-tannins, while to the other, half of the extracted residue (a proportionate part) was added, the whole was digested over night at 80° in a closed flask, the liquor cooled, filtered, and tannins and non-tannins determined as before. The results were corrected for dilution by the water added in the wet residue. For comparative results, a parallel analysis was made of extracts by digesting the substance over night at 80° according to the official method. The results were as follows:

The results in columns 1 and 2 of the following table all show a reabsorption of tanning materials by the extracted residues, being greatest in the case of canaigre. The enormous loss with this material may be partly due to the presence of starch, which also reprecipitates tanning materials. The reprecipitation noted in columns 1, 2 and 3 explains the advantage of percolation over the official digestion method of extraction, as shown in columns 4 and 5.

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PERCENTAGES OF EXTRACTS.

Samples	In original percolate	In percolate redigested with extracted residue	Difference due to absorption of tannins	In extract obtained by official method	Advantage of percolation over official method
Twenty grams oak bark percolated to 500 cc. in four hours at 80°C. :					
Tannins	10.99	9.98	1.01	9.68	1.31
Non-tannins	5.10	5.30	—	4.78	—
Ten grams hemlock bark percolated to 500 cc. iu five hours at 80°C. :					
Tannins	13.74	11.80	1.94	11.12	2.62
Non-tannins	3.94	4.63	—	4.13	—
Five grams of canaigre percolated to 500 cc. in eight hours at 50°C. :					
Tannins	41.27	[1]25.02	16.25	34.70	[2]6.57
Non-tannins	13.03	13.66	—	12.86	--

[1]This canaigre residue was digested with its liquor at room temperature.

[2]In this case the ground material was in contact with the liquor only two to three hours, at room temperature.

The action of starch and cellulose, respectively, in reprecipitating the tanning materials was observed by preparing a canaigre percolate, dividing into three portions, analyzing portion 1 as obtained, redigesting portion 2 in the cold with 1 gram of shredded filter paper, and redigesting portion 3 in the cold with 1 gram of bruised starch. Portions 2 and 3 were filtered, and in both cases a loss of tannins was observed.

PERCENTAGES OBTAINED.

Samples	Tanning materials in original percolate	After digestion with cellulose	Reabsorption by cellulose	After digestion with starch	Reabsorption by starch
No. 1510, old, red canaigre percolated at 50°C. ;					
Tannins	40.58	36.46	4.12	38.64	1.94
Non-tannins	12.72	13.04	—	13.90	-
No. 1511, young, yellow canaigre, percolated at 50°C. ;					
Tannins	31.98	28.50	3.48	30.24	1.74
Non-tannins	16.12	15.26	--	16.52	--

The cellulose shows a much stronger action than starch, the reprecipitation being about twice as great.

This suggests the inaccuracies introduced into analytical work by the use of filter papers. Our repeated experiments show that the first portions of tanning extracts filtered through paper contain noticeably less solids than the latter portions—the deficiency being found due to loss of tanning materials. In order to do away with this error I now use an asbestos filter made by placing a mat of prepared woolly asbestos in a porcelain strainer funnel, covering the mat with fine asbestos and drying the filter

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in an oven. By the use of this filter no loss of tanning materials occurs and the amount of total solids obtained is usually greater than in the last portions of the same liquors filtered through paper.

The effect of temperature upon completeness of extraction was shown by percolating oak, hemlock, and canaigre at different temperatures shown by the table.

PERCENTAGES OBTAINED.

Samples	Percolated at 55°C.	Percolated at 80°C.	Percolated at steam heat
Oak bark:			
Tannins	9.01	10.99	10.69
Non-tannins	4.44	5.10	6.75
Hemlock bark:			
Tannins	10.73	13.74	15.69
Non-tannins	3.58	3.94	8.22
Canaigre, old roots:			
Tannins	41.27	—	41.74
Non-tannins	13.03	—	17.84
Canaigre, young roots:			
Tannins	31.67	—	30.68
Non-tannins	16.25	—	28.56

It is seen that the extraction of oak bark is complete at 80°, while hemlock, owing probably to the difficultly soluble reds, yields more extractives by continuous percolation at the higher temperature. The extraction of canaigre is complete at 50° to 55° C. It is, in fact, not possible to make a satisfactory percolation of this material above this point, since the starch then swells and clogs up the Sohxlet tube.

The percolations of canaigre at steam heat, noted in the table, were made by placing the material in a thin layer on an asbestos mat in a large continuous copper extractor. The increase in 1510 of non-tannins from 13.03 per cent. to 17.84 per cent., and in 1511 from 16.25 per cent. to 28.56 per cent. is due to the solution of starch, whose presence in the extract causes turbid filtrates and is therefore an element of inaccuracy.

The above observations show—

(1) That in the extraction of barks, wood, leaves, etc., a percolation method is essential to complete extraction, owing to the reabsorption of tanning materials by cellulose, starch, albuminoids, etc.

(2) That the percolation method must be modified to suit the material under examination. Continuous extraction at steam heat will probably manage most woody materials, but canaigre requires to be percolated at 50° to 55° C., at which point extraction is complete, and we avoid the solution of starch, which does not properly belong with soluble non-tanning materials and whose presence is a source of inaccuracy in determining tannins.

(3) In accurate work the use of an asbestos filter is necessary, the loss of tanning materials in the filter thus being avoided.

(4) The following method of extraction for canaigre is recommended: A Sohxlet extractor is fitted inside with a 100 mesh brass gauze

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disk which is pushed nearly to the bottom of the tube, and a mat of woolly asbestos, previously extracted with hot hydrochloric acid, is deposited on the gauze. The mat is then covered with fine asbestos, the prepared extractor is placed in a sheet-metal tank of suitable size and 8 to 10 inches deep, the bottom of which is perforated with holes which receive the rubber stoppers through which the lower ends of the Soxhlets project. The tank is then filled with water at 50° C., and kept at that point by a small flame. The extractor is then partly filled with water and 5 grams of canaigre are floated into the extractor. A tightly fitting rubber stopper carrying a 250 to 500 cc. funnel is then fitted to the top of the Sohxlet, the funnel is filled with water and the stopcock turned so that the percolate will run to 500 cc. in four hours. The percolate is allowed to cool, made to the mark, shaken, an aliquot taken for total solids, the remainder filtered through an asbestos filter and soluble solids and tanning materials determined as usual.

(5) In conclusion, it is advisable that a more detailed examination of the percolation method, as applied to different materials, be made, and the best temperature for each one determined, as it is certain that any particular temperature can not be fixed upon for all substances alike.

REPORT ON TANNINS.

I. H. Yocum, Referee.

Bulletin No. 56 U. S. Dept. Agric.

The comparative work on tannins during the past year is of considerable interest, inasmuch as there are no less than twenty individuals contributing, and in addition to the results obtained on the samples sent out, Messrs. Carr, Forbes, Eachus, and Alsop present some interesting data relative to the methods, which are embodied in this report.

Two lots of samples were sent out, the first at the beginning of the year being a commercial chestnut-wood extract and a hemlock liquor, and with these were sent two makes of hide powder, one from Vienna and the other from Ridgway, Pa.

It was requested that the official method be followed, and that if other than the official method were in use by the collaborator results by it be also sent in. The hemlock liquor was thoroughly filtered before being sent out, and showed no precipitate at 40° F. and contained no reds at the time of shipment.

The second lot of samples was an extract made by the referee from grape sugar and gallotannin and contained no precipitate when shipped, but upon standing some three months did precipitate some insoluble material. The reports, however, were all in before this was noticed, and it is not probable that there was any insoluble material in this extract when the various analyses were made. Vienna hide powder was sent with this sample.

The results obtained are as follows:

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CHESTNUT-WOOD EXTRACT

Name	Hide[1]	Moisture Per cent.	Total solids Per cent.	Soluble solids Per cent.	Non-tannins Per cent.	Tannins Per cent.	Reds Pr. ct.
Allaire	A	59.59	40.41	38.45	14.05	24.40	1.96
	B	——	——	——	14.34	24.11	
Alsop	A	59.17	40.56	37.99	13.75	24.24	2.57
	B	——	——	——	13.69	24.30	
Carr	A	59.49	40.53	37.66	15.53	22.13	2.87
	B	——	——	——	15.72	21.94	
Eachus	A	59.17	41.06	39.14	14.21	24.93	1.92
	B	——	——	——	14.36	24.78	
Eitner (Weiss)	A	58.16	41.84	40.89	14.45	26.14	0.95
	B	——	——	——	14.55	26.34	
Forbes	A	58.22	41.48	40.12	13.92	26.20	1.36
	B	——	——	40.09	13.86	26.23	1.39
Haley	A	58.96	41.04	38.62	13.88	24.74	2.42
	B	——	——	——	14.06	24.56	
Hurty	A	58.11	41.89	39.38	14.87	24.51	2.51
	B	——	——	——	14.80	24.58	
Krug	A	59.60	41.05	39.54	14.16	25.38	1.51
	B	——	——	——	14.78	24.76	
Lowell	A	58.15	41.85	39.50	14.65	24.85	2.35
	B	——	——	——	14.75	24.75	
McDowell	A	58.95	40.87	38.70	14.03	24.67	2.17
	B	——	——	——	14.64	24.06	
Procter	A	58.97	41.03	38.10	15.55	22.55	2.93
	B	——	——	——	15.30	22.80	
Small	A	59.21	40.72	38.22	14.57	23.65	2.50
	B	——	——	——	14.22	24.00	
Tiffany	A	58.89	41.11	38.97	13.46	25.51	2.14
	B	——	——	——	13.69	25.28	
Westenfelder[2]	——	59.05	41.44	38.96	14.33	24.63	2.99
Parker[2]	A	——	——	40.10	12.20	27.90	
	B	——	——	——	14.30	25.80	
Touse[2]	A	——	——	40.16	12.25	27.91	
	B	——	——	——	14.50	25.66	
Yocum	A	59.20	40.59	38.20	13.61	24.59	2.39
	B	——	——	——	13.92	24.28	
Mean	A	58.89	41.07	38.98	14.31	24.67	2.09
Maximum	A	59.60	41.89	40.89	15.55	26.44	2.93
Minimum	A	58.11	40.41	37.66	13.46	22.13	0.95
Mean	B	——	——	——	14.52	24.46	
Maximum	B	——	——	——	15.72	26.34	
Minimum	B	——	——	——	13.69	21.94	
Maximum difference from minimum	A	1.49	1.48	3.23	2.09	4.31	1.98
	B	——	——	——	2.03	4.40	
Maximum difference from mean	A	0.71	0.82	1.91	1.24	2.54	1.14
	B	——	——	——	1.20	2.52	

[1] Hide powder "A" was the Vienna product; hide powder "B" was the Ridgway product.

[2] Not having followed official method, are not included in average.

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Hemlock Liquor

Name	Hide[1]	Total solids Per cent.	Soluble solids Per cent.	Non-tannins Per cent.	Tannins Per cent.	Reds Pr. ct.
Allaire	A	4.57	4.44	2.02	2.42	0.13
	B	—	—	2.10	2.34	—
Alsop	A	4.72	4.57	2.20	2.36	0.15
	B	—	—	2.12	2 45	—
Carr	A	4.63	[2]4.63	2.32	2.31	—
	B	—	—	2.35	2.28	—
Eachus	A	4.78	4.68	2.13	2.55	0.10
	B	—	—	2.22	2.44	—
Eitner (Weiss)	A	4.77	4.63	2.16	2.47	0.14
	B	—	—	2.18	2.45	—
Forbes	A	4.69	4.67	2.14	2.53	0.02
	B	—	—	2.18	2.49	—
Haley	A	4.83	4.63	2.35	2.28	0.20
	B	—	—	2.17	2.46	—
Krug	A	4.54	4.48	2.16	2.32	0.06
	B	—	—	2.13	2.35	—
Lowell	A	4.84	4.74	2.20	2.54	0.10
	B	—	—	2.24	2.50	—
McDowell	A	4.74	4.63	2.18	2.45	0.11
	B	—	—	2.23	2.40	—
Procter	A	4.72	4.53	2.25	2.28	0.19
	B	—	—	2.24	2.29	—
Small	A	4.64	4.55	2.16	2.39	0.09
	B	—	—	2.17	2.38	—
Yocum	A	4.71	4.66	2.14	2.52	0.05
	B	—	—	2.13	2.53	—
Parker	A	4.80	[2]4.80	2.00	2.80	—
	B	—	—	2.20	2.60	—
Mean	A	4.71	4.60	2.17	2.43	—
Maximum	A	4.84	4.74	2.35	2.55	0.19
Minimum	A	4 54	4.44	2.00	2.28	0 02
Mean	B	—	—	2.19	2.41	—
Maximum	B	—	—	2.35	2.53	—
Minimum	B	—	—	2.10	2.28	—
Maximum difference from mean	A	0.17	0.16	0.18	0.15	0.09
	B	—	—	0.16	0.13	—

[1] Hide powder "A" was the Vienna product, hide powder "B" was the Ridgway product.

[2] Not filtered for soluble solids and hence not included in averages of soluble solids and tannins.

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THEORETICAL EXTRACT

Name	Moisture Per cent.	Total solids Per cent.	Soluble solids Per cent.	Non-tannins Per cent.	Tannins Per cent.	Reds Per ct.	Red tannin Per ct.
Alsop.....	61.20	38.82	37.32	19.18	18.14	1.50	19.64
Carr.....	61.97	37.91	[1]37.91	18.66	19.25	—-	19.25
Eachus.....	61.60	38.43	37.42	18.90	18.52	1.01	19.53
Forbes	60.57	39.43	[1]39.43	19.04	20.39	——	20.39
Haley	60.69	39.23	37.46	18.64	18.82	1.77	20.59
Hurty.....	60.73	39.27	38.33	18.89	19.44	0.94	20.38
Kerr	60.01	39.99	38.33	21.41	16.92	1.66	18.58
McDowell.....	60.94	38.72	37.50	19.12	18.38	1.22	19.60
Nichols	61.35	38.65	36.88	18.68	18.20	1.77	19.97
Small	61.99	38.09	36.95	17.50	19.45	1.14	20.59
Yocum	61.05	38.20	36.80	17.90	18.90	1.40	20.30
Mean	61.10	38.79	37.44	18.90	18.54	1.35	19.89
Maximum...	61.99	39.99	38.33	21.41	20.39	1.77	20.59
Minimum...	60.01	37.91	36.80	17.50	16.92	0.94	18.58
Maximum difference from minimum .	1.98	2.08	1.53	3.91	3.47	0.83	2.01
Maximum difference from mean	1.09	1.20	0.89	2.51	1.85	0.42	1.31
Theoretical content of sample....	62.23	37.77	37.77	17.58	20.19	——	20.19

[1] Not filtered for soluble solids, hence not included in averages of soluble solids or tannins.

NOTE—Hide powder was the Vienna product.

Mr. Pierre Allaire states that the official method was followed; that he considers hide powder "A" a little better than "B," and that he did not obtain a perfectly clear non-tannin filtrate from the extract. Mr. B. Weiss made the analysis of the sample sent to Mr. Eitner of the Vienna Research College for the Leather Industries. He states that he pursued the official method, and also reports his results from the filter-tube method. He obtained 13.90 per cent. non-tannins on the chestnut-wood extract and 2.13 per cent. non-tannins on the hemlock liquor by following the filter-tube method.

Dr. Hurty obtained 41 per cent. total solids, 39.68 per cent. soluble solids, 15.50 per cent. non-tannins, and 24.18 per cent. tannins by a method he published sometime ago in the Leather Manufacturer.

W. C. Tiffany: "Our method varies from the official in that we employ 10 instead of 15 grams dry hide powder, and we shake three times, using one-third of the hide powder each time." He reports from this method 41.11 per cent. total solids and soluble solids--non-tannins from "A" hide powder, 12.32; "B," 12.90—giving respectively, 28.79 per cent. and 28.21 per cent. tannins.

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Mr. Kerr states that the sample of grape sugar and gallotannin was clear and light brown in color when received, but before being analyzed was covered with a luxuriant growth of mold. He doubts the value of his results in consequence.

M. S. McDowell: "The extract (grape sugar and gallotannin) when dissolved made a clear solution, but upon filtering through S. & S. paper 1.22 per cent. were removed. Am of the opinion that in all cases there is an absorption, greater or less, by the cellulose of the filter paper."

Mr. Lowell reports on the chestnut-wood extract 15 per cent. non-tannins and on the hemlock liquor 2.23 per cent. non-tannins by following the official method and using the kind of hide powder employed in his laboratory, which contained 0.0070 gram of material soluble in water, as per directions for obtaining same.

Mr. Kerr states that by using his laboratory hide powder, which contained 0.0080 gram soluble material, he obtained 21.41 per cent. non-tannins from the grape-sugar extract.

Dr. J. Gordon Parker reports results obtained by Herolds Institute method: tannins 28.90 per cent., non-tannins 12.10 per cent., solids 40.10 per cent. on the chestnut-wood extract; and tannins 2.80 per cent., non-tannins 2 per cent., solids 4.80 per cent. on the hemlock liquor. He states: "You will notice that they (the analyses he reports) are all done by the hide-filter method. * * * None of the hide powders has been washed, as you instructed, an ordinary analysis being made according to the method laid down by the international association with Procter's form of hide filter, 5 grams of powder being used in each case. Mr. Touse, my colleague, employed the same process."

Dr. H. R. Procter: "The method appears to be a good one, and the two hide powders give very concordant results; but I do not know that it is better than the 'International,' while the results are in every case lower. I do not regard this as a defect, though it is impossible with our present knowledge to say that either give the absolute percentage of tanning, or one more than the other."

By the "International" filter-tube method he obtains on the chestnut-wood extract: tanning matter 27.9 per cent., non-tannins 11.8 per cent., insoluble at 60° F. 1.9 per cent., water 58.4 per cent. By the Yorkshire College shake method: tanning matter, Vienna hide 24.1 per cent., Buffalo hide 22.4 per cent.; non-tannins, Vienna hide 15.6 per cent., Buffalo hide 17.3 per cent. In this last method the powder is added in three successive portions, 6 grams powder used and 100 cc. of liquor. The Buffalo powder is coarse-ground dry hide, heavy, granular, and unsuitable for the filter-tube. In the filter method the first 30 cc. passing through are thrown away, the next 50 cc. evaporated for non-tannins. On the hemlock liquor, by the "International" method, Dr. Procter obtained tanning matter 2.45 per cent., non-tannins 2.16 per cent.; and by the Yorkshire method, tanning matter 2.25 per cent., non-tannins 2.35 per cent., results being identical from both Vienna and Buffalo hide.

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Dr. Forbes reports non-tannins obtained by the use of Fiebing's hide powder in the chestnut-wood extract 13.15 per cent.; in the hemlock liquor 2.05 per cent., and in the grape-sugar extract 19.05 per cent. All filtrations were done through No. 597 S. & S. paper, and all dryings at 100° C.

E. J. Haley finds 14.28 per cent. non-tannins in the chestnut-wood extract from a hide powder of his own make. He reports the ash analysis of the two hide powders sent out:

	"A" hide Per cent.	"B" hide Per cent.
Ash	0.19	0.36
Lime	0.06	0.05
Alumina	Trace	Trace
Ferric oxid	Trace	Trace

Mr. F. H. Small reports that his laboratory method does not vary from the official to any extent and hence does not report from it.

Mr. B. D. Westenfelder: "I did not follow directions you sent out, but used my laboratory method. It is as follows: Dissolve in water at 40° C. in a 500 cc. flask; place on water bath for fifteen minutes and agitate frequently; fill to mark with cold water; cool rapidly in cold water and make up to 1 liter; filter through 20 cm. double-folded S. & S. No. 6298 filter paper; discard first 100 cc. that passes through; refilter then till absolutely clear.

Wash hide powder with water containing acid sodium sulphite and sulphuric acid, then wash till absolutely free from soluble hide and saline matter, squeeze and shake. All residues dried in air oven at 104° to 106° C. for two hours." His results are:

	Chestnut-wood extract Per cent.	Hemlock liquor Per cent.	Grape-sugar extract Per cent.
Solids	41.95	4.57	39.80
Soluble solids	38.96	4.57	39.80
Non-tannins:			
No. 1	13.07	2.13	19.53
No. 2	14.33	2.13	19.83

Non-tannin No. 1 wet hide powder was added, in two portion of 25 grams each; 50 grams wet hide total used. Non-tannin No. 2, 50 grams wet hide added at once, 200 cc. of liquor used for shaking and 100 cc. evaporated; wet hide powder contained 78 per cent. moisture. In the case of the liquor only 40 grams of wet hide were used.

Mr. Oma Carr states that at 25° C. he obtained 2.09 per cent. of reds in the chestnut-wood extract, and at 10° C. 3.66 per cent. reds, an increase of 1.57 per cent. He also states that at 25° C. the hemlock liquor was clear, but at 10° C. he found 0.20 per cent. of reds. By dissolving an extract according to the method (20 grams to the liter), and by dissolving it so that it will make a liquor of 1.02 sp. gr., he finds:

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	Official Per cent.	At 1.02 sp. gr. Per cent.	Difference Per cent.
Total solids	40.63	40.43	0.10
Soluble solids	37.66	37.38	0.28
Reds	2.87	3.05	0.18
Tannin	22.03	21.71	0.32
Non-tannins	15.63	15.66	0.03

This liquor of 1.02 sp. gr. gave soluble solids, at 25° C. 37.38, and at 8° C. 35.94, a difference of 1.44. Mr. Carr presents the following data regarding the drying of the grape-sugar extract:

DRIED IN AIR AT 100° C.

Solids (direct)			Solids (indirect)			Non-tannins		Tannins	
Time	Interval	Per cent.	Time	Interval	Per cent.	Time	Interval	Per cent.	Per cent.
2	——	40.46	3	——	39.26	——	——	——	——
4	2	40.00	——	——	——	——	——	——	——
10	6	39.04	——	——	——	——	——	——	——
12	2	38.99	——	——	——	16	——	19.67	——
28	16	38.48	24	21	38.28	24	8	19.46	18.82
32	4	38.35	——	——	——	——	——	——	——
50	18	38.03	42	18	37.91	45	21	18.66	19.25
56	6	37.93	50	12	37.81	64	19	18.10	19.71
96	40	37.51	90	40	37.22	112	48	17.22	20.00
136	40	37.29	138	48	36.99	136	24	16.92	20.07
Theoretical contents of sample	——	——	——	——	37.77	——	——	17.58	20.19
Maximum decrease	3.17	——	——	——	2.27	——	——	2.75	——

"The non-tannins show a rate of decomposition about twice as great as the solids as a whole—precisely as it should be, considering that the non-tannins are largely left handed sugars.

"The absurdity of drying five days without constant weight is manifest. In my opinion, the water is wholly expelled from residues of 500 milligrams or less inside of four hours and any loss thereafter is chargeable to decomposition. These sugars of the dextrose order do not oxidize appreciably, while their rate of decomposition is wholly dependent upon the temperature used in their dehydration. It is possible to select from the above table percentages in fair accordance, but I hold that such arbitrary selection is absolutely without apology where the rate of decrease continues thereafter, whether more slowly or not.

"It seems to me wisely consistent with the best interest of the method to stipulate that extracts and other materials containing large quantities of invert sugars must be dried in vacuo at 70° C. The theoretical sample has served the exceedingly useful purpose of proving the inapplicability of ordinary dehydration methods to its desiccation. If the objection be made

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that chemists are not supplied with means of vacuum drying, it is a wholly consistent thing to require them to provide it. In the analysis of sugar, ore, milk, etc., the means have been adapted to the method, and the polariscope, assay balance, and Babcock machine are essentials.

"When it comes thus to a choice between a method vitally defective and one in which special apparatus must be provided, which is necessary in the operation of a method which has the advantage of accuracy, there seems hardly room for debate."

Mr. Eachus presents the following data on drying:

"Twelve portions of 100 cc. of well-mixed extract solution (20 grams to the 100 cc.) were evaporated to dryness. Six of these were dried on the top shelf of a hot-air oven; the other six were dried on the bottom shelf of the same oven. At the end of three hours one dish from each shelf was weighed, and at one hour intervals thereafter a dish was weighed from each shelf. The temperature of the top shelf was 100° C., and of the bottom shelf 125° C.

"Twelve portions of 100 cc. of non-tannins from the same solution were treated similarly.

	Solids			Non-tannins		
Time	100° C., top shelf Gram.	125° C., bottom shelf Gram.	Difference Gram.	100° C., top Gram.	125° C., bottom Gram.	Difference Gram.
After 3 hours	0.8399	0.8218	0.0181	0.3036	0.2843	0.0193
After 4 hours	0.8275	0.8152	0.0123	0.3052	0.2842	0.0210
After 5 hours	0.8280	0.8111	0.0169	0.3051	0.2855	0.0196
After 6 hours	0.8247	0.8099	0.0148	0.3044	0.2842	0.0202
After 7 hours	0.8244	0.8009	0.0235	0.3027	0.2820	0.0207
After 8 hours....	0.8283	0.8027	0.0256	0.3072	0.2863	0.0209
Average.....	———	———	0.0185	———	———	0.0203

"From this it is seen that variations are due to drying at various temperatures and that a constant weight is obtained by drying at 100° C. for from four to eight hours, but that a loss of non-tannins occurs by drying at 125° C. both in the total solids and non-tannin determinations, probably due to decomposition of the non-tannins. Variations in temperature within these limits affect the non-tannins largely without any considerable action upon the tannins. Variations then in drying tannin solutions are a function of the temperature, although no doubt long-continued drying at 100° C. would occasion oxidation of the tannin.

"Fourteen analyses of an extract were made and the drying done in various ways, always making it a point to dry the soluble solids and non-tannins under identical conditions and side by side in the drying oven.

"I would suggest that for the sake of unformity the time and temperature of drying be closely defined for the method; but I think my results show that the per cent. of tannins is not largely influenced by variations in drying among various operators, provided they dry soluble solids and non-tannins under the same conditions at all times.

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Dried on—	Weight of soluble solids Gram.	Weight of non-tannins Gram.	soluble solids Pr. ct.	Non-tannins Pr. ct.	Tannins Pr. ct.
Top shelf hot-air oven, 4 hrs. at 100° C	0.8686	0.4426	43.43	26.12	17.31
Top shelf hot-air oven. 8 hrs. at 100° C	0.8657	0.4400	43.29	25.96	17.33
Bot. shelf hot-air oven, 4 hrs. at 125° C	0.8306	0.4131	41.53	24.37	17.16
Bot. shelf hot-air oven, 8 hrs. at 125° C	0.8366	0.4117	41.83	24.29	17.54
Top shelf water oven, 4 hrs. at 90° C	0.8641	0.4422	43.21	26.09	17.12
Top shelf water oven, 8 hrs. at 90° C	0.8718	0.4500	43.59	26.55	17.04
Top shelf water oven, 18 hrs. at 90° C	0.8630	0.4439	43.15	26.20	16.95
Sec. shelf water oven, 8 hrs. at 90° C	0.8703	0.4469	43.52	26.37	17.15
Sec. shelf water oven, 18 hrs. at 90° C	0.8630	0.4443	43.15	26.22	16.93
Third shelf water oven, 8 hrs. at 90° C	0.8682	0.4484	43.41	26.46	16.93
Third shelf water oven, 18 hrs. at 90° C	0.8654	0.4392	43.27	25.91	17.36
Bot. shelf water oven, 4 hrs. at 90° C	0.8708	0.4462	43.54	26.33	17.21
Bot. shelf water oven, 8 hrs. at 90° C	0.8695	0.4468	43.48	26.37	17.11
Bot. shelf water oven, 18 hrs. at 90° C	0.8616	0.4396	43.08	25.94	17.14

"The data I present seem to prove that the changes in weight of soluble solids and non-tannins are the same under the same conditions, and that, so far as the tannins are concerned, there is no difference in the time necessary for complete dehydration. It is only necessary, therefore, to define the time and temperature to be used."

Mr. Forbes states that after a careful investigation he found that no matter how long tanning liquor was passed through filter paper there was a slow but appreciable absorption of tanning matter; but that with an asbestos mat the absorption was nil. He communicated with the paper makers, but states that they failed to make a satisfactory paper from this material.

Mr. Forbes calls attention to the temperature of extraction of raw materials, the results shown by him in the paper read before this society last year on canaigre extraction, Bulletin No. 51, and the work of Procter and Parker on various other materials on the same subject, and asks that this subject be given special attention.

Mr. Alsop presents the following data on the absorption of tanning matter by paper and kaolin:

A solution of gallotannin free from precipitate was continually filtered through S. & S., No. 570, 15 cm. filter paper, care being taken on the duplicates to have the paper weigh the same.

Original solids	First solution, 0.8147 gram. to 100 cc. Gram.		Second solution, 0.8182 gram. Gram.	
First, 125 cc. passing through	0.7905, loss	0.0242	0.7979, loss	0.0203
Second, 125 cc. passing through	0.8054, loss	0.0093	0.8117, loss	0.0065
Third, 125 cc. passing through	0.8077, loss	0.0070	0.8093, loss	0.0089
Fourth, 125 cc. passing through	0.8085, loss	0.0062	0.8169, loss	0.0013
Fifth, 125 cc. passing through	——	——	0.8266, loss	0.0016
Sixth, 125 cc. passing through	——	——	0.8146, loss	0.0036

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Ten grams kaolin were then thrown on the wet paper; on the first after 500 cc. had passed through, on the second after 750 cc. had passed through:

Original solids	First solution Gram.	Gram.	Second solution Gram.	Gram.
First, 125 cc.	0.7996, loss	0.0151	0.8174, loss	0.0008
Second, 125 cc.	——	——	0.8153, loss	0.0029

By filtering with 10 grams kaolin on dry filter paper:

Original solids	First solution Gram.	Gram.	Second solution Gram.	Gram.
First, 125 cc.	0.7567, loss	0.0580	0.7705, loss	0.0477
Second, 125 cc.	0.7969, loss	0.0178	0.8075, loss	0.0107

By filtering a hemlock liquor, free from precipitate, under the same conditions:

Original solids	0.6378 gram. per 100 cc. Gram.	Gram.
First 125 cc. passing through	0.6225 per 100 cc. loss	0.0153
Second, 125 cc. passing through	0.6299 per 100 cc. loss	0.0079
Third, 125 cc. passing through	0.6354 per 100 cc. loss	0.0024
Fourth, 125 cc. passing through	0.6347 per 100 cc. loss	0.0031
Fifth, 125 cc. passing through	0.6344 per 100 cc. loss	0.0034
Sixth. 10 grams kaolin added	0.6179 per 100 cc. loss	0.0199
Seventh, 10 grams kaolin added	0.6245 per 100 cc. loss	0.0133
Eighth, 10 grams kaolin added	0.6388 per 100 cc. gain	0.0010

Ten grams kaolin on dry paper with this liquor gave:

Original solids	0.6378 gram. per 100 cc. Gram.	Gram.
First, 125 cc. passing through	0.6023 per 100 cc. loss	0.0355
Second. 125 cc. passing through	0.6280 per 100 cc. loss	0.0098
Third, 125 cc. passing through	0.6322 per 100 cc. loss	0.0056

This procedure was followed on extract solutions which had been filtered clear:

	Twenty grams to liter Gram.	Gram.	Ten grams to liter. Gram.	Gram
Original solids	0.8287	——	0.4085	——
First, 125 cc. passing through	0.8175, loss	0.0112	0.4034, loss	0.0051
Second, 125 cc. passing through	0.8215, loss	0.0072	0.4069, loss	0.0016
Third, 125 cc. passing through	0.8237, loss	0.0050	0.4081, loss	0.0004
Fourth, 125 cc. passing through	0.8233, loss	0.0054	0.4100, gain	0.0015
Fifth, 125 cc. passing through	0.8286, loss	0.0001	——	——
Sixth, 10 grams kaolin added	0.8035, loss	0.0252	0.3895, loss	0.0190
Seventh, 10 grams kaolin added	0.8199, loss	0.0088	0.4041, loss	0.0044
Eighth, 10 grams kaolin added	——	——	0.4098, gain	0.0013

Ten grams kaolin on paper dry.

	Twenty grams to liter Gram.	Gram.	Ten grams to liter Gram.	Gram.
First, 125 cc. Passing through	0.7822, loss	0.0465	0.3825, loss	0.0260
Second, 125 cc. passing through	0.8262, loss	0.0025	0.4004, loss	0.0081

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The variations due to two kinds of filter paper are shown by the subjoined data. No. 602 S. & S. 15 cm. is a hard-finished heavy paper while No. 590 S. & S., 15 cm. is a soft-finished light paper. The extract used on this was the sample of grape-sugar and gallotannin sent out by the referee. The official method of filtration was pursued, and the results are given under No. 1 and under No. 2; 150 cc. of solution were thrown away and then 100 cc. passed through the filter and evaporated.

	Number 1		Number 2	
	Gram	Gram	Gram	Gram
Original total solids	0.7685	——	0.7685	——
No. 590 paper	0.7483, loss	0.0202	0.7622, loss	0.0063
No. 602 paper	0.7106, loss	0.0579	0.7585, loss	0.0100
No. 590 paper, 10 grams kaolin	0.7286, loss	0.0399	0.7600, loss	0.0085

These results show that under the present official method a certain amount of tannin is reported as reds and that by passing 150 cc. of the solution through the paper before taking the 100 cc. for soluble solids most of the error due to the absorption of the paper and also of the kaolin is obviated. It also shows that different kinds of paper absorb different amounts of tanning material. It will be seen by looking over these data that the absorption by the paper is considerable, but that upon continued contact of the paper and tan liquor the paper's affinity is satisfied. The extreme slowness of filtration that ensues from passing tannin solutions through the filter until the affinity of the paper is completely satisfied makes it impractical in the method, but since the error is quite small after 150 cc. have passed through, I would suggest that the method in this particular, adopted by the International Association, be embodied in the official method, except in regard to the paper, where 590 S. & S., 15 cm. should be substituted for 602 S. & S. paper. This makes the directions for filtration read: "Filtrations shall take place through S. & S., No. 590, 15 cm., and the first 150 cc. passing through shall be rejected. Where a clear filtrate can not otherwise be obtained, the use of about 10 grams of kaolin previously washed with a portion of the tannin solution is permissible, but is to be noted in the report." "While this does not entirely obviate the difficulty, it leaves a very small error due to this cause and seems the only practical way out."

The soluble material in the hide and the quantity of dry hide used are presented in the following table. Hide "A" is that sent out with the first sample marked "A," Vienna hide; "B" is that sent out with first sample marked "B," Ridgeway hide; "C" is that sent out with the second sample and is Vienna hide.

The samples are, No. 1, chestnut-wood extract; No. 2, hemlock liquor, and No. 3, grape-sugar and gallotannin extract.

In no case does the soluble material in the hide powders exceed the limits of the method.

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TABLE 4.—SOLUBLE MATERIAL IN AND QUANTITY OF DRY HIDE USED.

Name	Solubles in hide "A" Gram.	"B" Gram.	"C" Gram.	Dry hide No. 1 sample "A" hide Gram.	Dry hide No. 1 sample "B" hide Gram.	Dry hide No. 2 sample "A" hide Gram.	Dry hide No. 2 sample "B" hide Gram.	Dry hide No. 3 sample hide Gram.
Allaire.....	0.0070	0.0075	——	15.43	13.98	12.99	12.55	——
Alsop.....	0.0025	0.0030	0.0026	12.00	12.00	12.00	12.00	12.00
Carr.....	0.0050	0.0100	——	16.50	16.50	14.75	14.75	——
Eachus.....	0.0020	0.0035	0.0020	12.00	12.50	12.00	12.50	12.00
Eitner(Weiss)	——	——	——	12.42	11.97	12.42	11.97	——
Forbes.....	0.0030	0.0028	0.0025	11.48	10.14	13.05	11.89	——
Haley	0.0040	0.0020	0.0010	12.40	13.20	9.30	9.90	11.20
Hurty	0.0039	0.0041	0.0066	11.37	12.23	11.77	14.39	——
Krug	0.0061	0.0039	——	——	——	——	——	——
Kerr.....	——	——	0.0065	——	——	——	——	11.15
Lowell.....	0.0026	0.0046	——	11.73	11.95	10.56	11.83	——
McDowell ..	0.0070	0.0090	0.0030	13.92	15.12	11.84	12.60	11.55
Nichols.....	——	——	0.0070	——	——	——	——	——
Proctor.....	0.0050	0.0040	——	10.50	12.24	12.81	13.47	——
Small.....	0.0026	0.0022	——	11.44	11.90	12.88	11.82	11.52
Tiffany	0.0100	0.0060	——	12.35	12.50	——	——	——
Yocum	0.0030	0.0040	0.0030	12.00	11.50	11.50	11.50	12.00

In the table of results on the chestnut-wood extract the difference between maximum and minimum of solids is 1.48 per cent. This is wholly due to variations in drying. The difference in soluble solids is 3.23 per cent. Assuming that the drying variations are the same as for solids, then the variation due to filtering is 1.75 per cent. The differences on non-tannins is 2.09 per cent. On the above assumption that 1.48 per cent. difference is due to drying, then 0.61 per cent. is the difference in the non-tannin determination proper. From this it is readily seen that drying and filtering are the greatest sources of variations in the tannin determination.

The hemlock liquor sent out as a sample was free from insoluble matter, yet there was reported a mean of 0.11 per cent. of reds, which was undoubtedly due to an error in the method for determining them. The same thing occurs in the grape-sugar—gallotannin extract, which contained no reds, yet was reported as containing on the average 1.35 per cent.; the sum of the reds and tannins, 19.89, being nearly the same as the theory for tannin in this sample, 29.19 per cent. Theory gave 37.77 per cent. solids, the mean of the results 38.79, a difference of 1.02 per cent., due to incomplete drying, no doubt. On non-tannins, theory gave 17.58 per cent., the mean of the results 18.90, a difference of 1.32, within 0.30 per cent. the same as the difference in solids, which was due to drying entirely. From these data I think it fair to conclude that the non-tannin determination is a satisfactory one, except in regard to drying.

There seems to be no question but that the cellulose of the filter paper removed tannin to the extent of a mean of 1.35 per cent. On the other hand, in many commercial extracts a complete removal of the reds

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is not effected by the directions of the method for filtering, the reds being such a fine precipitate that they practically all pass through the filter. Some means of obtaining a solution free of this precipitate, and yet not having the absorption of the paper enter into the determination, must be devised before the soluble solid determination will be satisfactory. Mr. Forbes suggested an asbestos filter paper, but this can not be obtained. Mr. Alsop suggests satisfying the affinity of the paper for tannin by passing 150 cc. through, and the use of kaolin, washed in the tannin solution before use, as a means of obviating both difficulties. This seems to me the only feasible means of obtaining satisfactory results, but even by this a slight error will remain.

The results of the work of Messrs. Carr and Eachus in regard to drying show the difficulties and errors of the present system. Mr. Carr's suggestion "to dry in vacuo at 70° C." would, in all probability, be the most satisfactory if it could be generally pursued, but I doubt if such a proviso could be enforced.

With this same difficulty in the determination of water in sugar solutions, sirups, etc., this association has not adopted the vacuum apparatus.

The data presented by Mr. Eachus would lead one to believe that in this determination, if the solids be exposed to decomposition in drying under the same conditions as the non-tannins, the actual loss of weight in each will be such as to give the same results in tannins.

The variations due to the various ways of drying are shown in the following table:

[Water oven, temperature, 90° C.; time twenty-four hours. Air oven, temperature, 100° to 104° C.; time, four hours. Vacuum oven, temperature 100° C.; time, two and one-half hours; 20 inches vacuum.]

Sample	No. 1 Gram.	No. 2 Gram.	No. 3 Gram.
Water oven	0.8241	0.7177	0.7080
Air oven	0.8119	0.7063	0.6986
Vacuum oven	0.8224	0.7151	0.7056

It would seem that to obtain any degree of concordance it is necessary to have the method of drying outlined with considerable exactness, both in regard to time and temperature, and it would seem to your referee a fitting subject for the forthcoming year's investigation. For the present, drying for eight hours at 100° C. in an air oven or eighteen to twenty hours in a water oven at 90° C. seems the least objectionable.

In the direct determination of water in extracts, etc., it is essential that the extract be evenly deposited as a film on the bottom of the containing vessel. This is best effected by diluting in the vessel with about 25 cc. of water before evaporating. It seems better to make the directions read that 1 gram of solids will remain after drying, instead of, as now, "use 3 grams of the extract," for owing to the varying concentration of extracts sometimes the film is much too thick to dry well.

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On September 30, 1897, there was organized in London the International Association of Leather Trades' Chemists, whose object is the promotion and adoption of standard methods of tannin analysis. This association received the support of practically all the Continental and English chemists interested, and after a great deal of discussion they adopted the following method for tannin:

METHOD

Preparation

Liquid Extracts.—Liquid extracts shall be rapidly stirred and mixed immediately before weighing, which shall be done rapidly to avoid loss of moisture. Thick extracts which can not be otherwise mixed may be heated to 50° C., then stirred, and rapidly cooled before weighing.

Barks and Solid Tanning Materials.—The whole sample, or not less than 250 grams, shall be ground in a mill until it will pass a sieve of five wires per centimeter. Materials such as barks, divi-divi, etc., containing fibrous material, shall be sieved and proportionate parts of the fibrous substance and that passing through sieve employed.

Strength of Solution.—Such solutions shall be employed that, upon the evaporation of 100 cc. the residue shall amount to between 0.6 and 0.8 gram.

Solution of Liquid Extracts.—A sufficient quantity shall be weighed into a covered basin or beaker, from which it shall be washed into a liter flask with about 500 cc. of boiling water and well shaken, and the flask shall be filled nearly to the mark with cold water, the neck being covered with a small beaker; it shall be placed under a cold-water tap, or otherwise rapidly cooled to a temperature between 15° and 20° C. and made up to the mark, after which it shall be thoroughly mixed and imemdiately filtered.

Filtration.—Filtration shall take place through S. & S. filter paper No. 602. The first 150 or 200 cc. of the filtrate shall be rejected. Where a clear filtrate can not be otherwise obtained, the use of a little kaolin previously washed with a portion of the tannin solution is permissible.

Extraction of Solid Materials.—Such quantity shall be weighed as wil give an infusion of the strength already prescribed. Not less than 500 cc. of the infusion shall be extracted at a temperature not exceeding 50° C., after which the temperature shall be raised to 100° C. and the extraction continued till the percolate is free from tannin and the whole made up to 1 liter, the weaker portion being concentrated if necessary by evaporation.

Total Soluble Matter.—One hundred cc. of the clear filtered tanning solution shall be evaporated on the water bath and shall afterwards be dried in an air oven, to constant weight at a temperature of 100° to 105° C., or at a temperature not exceeding 100° C. in vacuo.

Determination of Non-tannins.—The filter-tube method shall be adopted provisionally.

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The Bell form of filter shall be employed. Not less than 5 grams of hide powder shall be used, and the filtrate shall be rejected so long as it gives a turbidity with a clear tannin solution. The filtrate may be used for the determination of non-tannins so long as it gives no reaction with hide-powder water (a clear solution of soluble gelatin from the hide). Fifty cc. or less quantity of detannized solution shall be evaporated on a water bath and dried as directed for soluble matter.

The main difference between this and the official method of this association is in the non-tannin determination. The results from the filter tube are invariably lower than those obtained by the shaker. Messrs. Weiss, Procter, Parker, and Touse report results on the chestnut-wood extract and hemlock liquor by this method.

	Extract Per cent.	Liquor Per cent.
Weiss, nontannin	13.90	2.13
Procter, nontannin	11.80	2.16
Parker, nontannin	12.10	2.00
Touse, nontannin	12.25	——
Weiss, tannins	25.24	2.50
Procter, tannins	27.90	2.45
Parker, tannins	28.00	2.80
Touse, tannins	27.91	——

It is hoped that the more general use of the shaker method abroad will convince the foreign chemist of its superiority and that it will be incorporated in their method.

The manufacturers of extract are varying the concentration of their product much more now than in the past, and as the present method calls for 20 grams of extract per liter the solids per 100 cc. working solutions vary considerably, and inasmuch as these variations in concentration influence the results on both non-tannins and soluble solids a more definite statement regarding quantity of material is necessary.

An extract diluted 20 grams to the liter, giving 1.0648 grams of solids per 100 cc. of solution, and the same extract dissolved so that 100 cc. of solution had 0.8000 gram solids, gave:

	Twenty grams to liter Per cent.	0.8 gram per 100 cc. Per cent.
Soluble solids	50.00	51.15
Non-tannins	19 44	18.46

Uniformity in the quantity of hide and strength of solution are both necessary for concordance in the results on non-tannins, as has been proven, and with the absolute definition of the quantity of solids per 100 cc. of solution and the use of a certain quantity of hide powder this error is eliminated.

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The directions for washing the hide powder as a preliminary to the non-tannin determination are quite complicated and lengthy. To determine if some better means could not be devised several experiments were carried on, and it was found that by using about twenty-five times as much water as hide, by weight, a very satisfactory washing could be effected by one treatment.

Twenty grams of hide and 500 cc. of water were used in the following tests; the hide was well stirred in a large beaker, fresh water was used, and the hide and water stood one hour for each washing:

	Gram.
First washing, 100 cc. evaporated	0.1014
Second washing, 100 cc. evaporated	0.0070
Third washing, 100 cc. evaporated	0.0061
Fourth washing, 100 cc. evaporated	0.0079

If the hide answer the tests outlined under Paragraph VIII of the method, the preparatory washing can be much simplified and one of the most tiresome and objectionable points of the method obviated.

Recommendations

You referee makes the following recommendations:

That Paragraph II of Method, "Quantity of material," shall read:

"In the case of bark and similar material use such quantity as will give about 0.8 gram solids per 100 cc. of solution, extract in Soxhlet or similar apparatus at steam heat for non-starchy materials. For canaigre and substances containing like amounts of starch use temperture of 50° to 55° C. until near complete extraction, finishing the operation at steam heat. In the case of extract weigh such quantity as will give 0.8 gram solids per 100 cc. of solution, dissolve in 900 cc. of water at 80° C., let stand twelve hours, and make up to 1,000 cc."

That Paragraph III shall read:

"Weigh 2 grams if it be an extract into a flat-bottomed dish not less than 2½ inches in diameter; add 25 cc. of water, warm slowly till dissolved; continue evaporation and dry."

That the following be inserted as IIIa:

"All dryings called for, after evaporation to dryness on water bath or others, shall be done by one of the following methods, the soluble solids and non-tannins being dried under similar, and so far as possible, identical conditions:

"A. For twenty-four hours at the temperature of boiling water in a steam bath.

"B. For eight hours at 100° to 103° C. in an air bath.

"C. To constant weight in vacuo at 70° C.

"State in report the method of drying pursued."

That Paragraph V shall read:

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"Filtration shall take place through a double folded filter (S. & S., No. 590), the first 150 cc. passing through shall be rejected, 100 cc. next passing through shall be evaporated and dried. When a clear filtrate can not be otherwise obtained the use of 10 grams of kaolin previously washed in a portion of the tanning solution is permissible. Evaporation during filtration must be guarded against."

That Paragraph VI shall read:

"Prepare 20 grams of hide by washing in a No. 7 beaker (Griffin) with 800 to 1,000 cc. of water, stir well and let stand one hour; filter the magma through linen, squeeze thoroughly by hand and remove as much water as possible by means of a press, etc." (From here the same as in Bulletin No. 51.)

That the following be inserted as VIIa:

"A. That the temperature of solutions shall be between 16° and 20° C. when measured or filtered.

"B. Dryings to be made in flat-bottomed dishes not less than 2½ inches in diameter."

REPORT ON TANNIN.

By Oma Carr, Referee.

Bulletin No. 62, U. S. Dept. Agric.

Owing to disappointment in not receiving a hide-powder suitable for the official method, the referee delayed sending out the samples for co-operative work until November 1. On that date samples of liquid oakwood extract and solid quebracho extract, selected as representing typical commercial materials, were sent to the collaborators. Reports were received from eight analysts, giving the results to be discussed in the following pages. Work done under the referee's direction will be entered first, to be followed by a tabulation of the collaborative analyses.

Soluble Solids

In nearly all tanning materials the anhydrides, gums, phlobaphenes, etc., grouped as insolubles, are present in the analysis solution in such state of fine division that filtrates, even through finest paper, will not effect complete removal. In such cases the method permits the use of kaolin, previously washed in a portion of the solution, with the view of "filling" the paper and thus obstructing the passage of the insoluble matter. While this procedure accomplishes the object of a clear filtrate, it is open to the objection that kaolin is of varying composition and that the increased time of contact with the paper increases the absorption and lowers the result as to soluble solids.

With the aim of overcoming the paper absorption, the referee tried various methods of mordanting the paper and coloring with a dye without much success beyond pointing the way for further experiment. The paper was saturated with a solution of gallotannic acid and struck with a

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basic dye. Looseness of attraction prevented a good result, and subsequent washing removed a large amount of color. Paper so prepared, however, possessed less absorption power than the untreated fiber and the filtering power remained good. Possibly further experiment may enable the paper makers to produce an absorption-free fiber. As the fiber of the paper acts basically in tannin attraction, it was thought that the addition of a volatile acid, inert as to chemical action on the constituents of the solution, might overcome the attraction. Experiments were conducted on a solution of oakwood extract, adding 0.36 gm. of acetic acid, in weak solution, to each 100 cc. before filtration, and passing through plain and pleated No. 590, 15 cm. paper.

EFFECT OF THE ADDITION OF ACETIC ACID

Volume of filtered solution taken for determination	Soluble solids: Plain paper Per cent.	Soluble solids: Pleated paper Per cent.
First 50 cc.	41.01	41.90
Second 50 cc.	41.17	41.95
Third 50 cc.	41.66	42.27

It will be noted that the rate of filtration was higher with the pleated paper.

The action of plain folded paper, without acid, is shown in the following table, and it will be seen that there was a decrease rather than an increase in the rate of filtration:

SOLUBLE SOLIDS OBTAINED WITHOUT THE ADDITION OF ACETIC ACID AND THE USE OF PLAIN FOLDED PAPER

Method of filtration and volume of filtered solution taken	Soluble solids Per cent.
75 cc. through, 50 cc. taken	41.07
75 cc. through same paper, 50 cc.	40.95
75 cc. through same paper, 50 cc.	40.79

The action of kaolin and barytes, with the same solution, and no acid gave the following results:

COMPARISON OF EFFECT OF KAOLIN AND BARYTES ON THE AMOUNT OF SOLUBLE SOLIDS OBTAINED

Method of filtration	Soluble solids Per cent.
150 cc. passed, then 5 gm. kaolin, washed in solution	39.52
150 cc. passed, then 10 gm. kaolin, washed in solution	37.31
150 cc. passed, then 5 gm. barytes, washed in solution	40.79
150 cc. passed, then 10 gm. barytes, washed in solution	40.49

The use of a 100 cc. solution, 0.02 gm. of lead acetate, 0.36 gm. of acetic acid, correcting for removal by lead and dilution, and filtering through No. 590, 15 cm., pleated paper, gave triplicate determinations, as follows: 41.92, 41.70, 41.85 per cent. soluble solids. The filtrates were brilliantly clear.

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Work was undertaken along the same lines with solid quebracho extract, with the following results:

COMPARISON OF EFFECT OF KAOLIN AND BARYTES ON THE AMOUNT OF SOLUBLE SOLIDS OBTAINED, USING PLAIN FOLDED PAPER

Method of filtration	Soluble solids Per cent.
150 cc. passed, then 5 gm. kaolin, washed in solution ..	79.82
150 cc. passed, then 10 gm. kaolin, washed in solution..	74.67
150 cc. passed, then 5 gm. barytes, washed in solution..	76.36
150 cc. passed, then 10 gm. barytes, washed in solution..	76.80

EFFECT OF THE ADDITION OF ACETIC ACID, USING PLEATED PAPER

Volume of filtered solution taken for determination	Soluble solids Per cent.
First 50 cc.	77.05
Second 50 cc.	76.82
Third 50 cc.	76.71

The filtrates were clear.

By the use of 100 cc. of solution, 0.02 gram lead acetate, filtered through asbestos, and corrected for lead removal and dilution, triplicate determinations were obtained as follows: 74.41, 74.38, 74.40 per cent. soluble solids. The filtrates were brilliantly clear.

The use of 100 cc. solution, 0.02 gm. lead acetate, 0.32 gm. acetic acid, filtered through No. 590, 15 cm., pleated, and corrected for removal by lead and dilution gave the following triplicate determinations: 74.95, 75.24, 75.15 soluble solids. The filtrates were brilliantly clear.

A review of these results develops the following conclusions:

(1) Filtration through paper, plain or pleated, without "assistants" does not totally remove insolubles.

(2) Absorption is largely a function of the time the solution is in contact with the paper, being less for free filtering and greater for viscous solutions.

(3) Acetic acid modifies the basic nature of the paper.

(4) It is possible to secure concordant results by the use of lead acetate, acetic acid, and paper.

(5) As the method stands for soluble solids, it gives low figures for the oakwood and high for the quebracho, and this will hold good in the comparison of any materials so differing.

The referee is of the opinion that results reported to this association in the past, and the experience of the International Association of Leather Trades Chemists, are ample support for the retention of Schleicher and Schüll, No. 590, 15 cm., for all filtrations. It will be found, however, in substituting the pleated for the simple folded form now stipulated, that the passage of the liquor is expedited and the absorption is reduced.

Finally, with reference to the subject of soluble solids, the referee would suggest the following optional method and the substitution of "barytes" for "kaolin" in the official method:

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To 100 cc. of the solution add 10 cc. of a solution of acetate of lead containing 4 grams of the salt per liter, adding the reagent drop by drop from a burette and stirring meanwhile. Now add 10 cc. of a solution of acetic acid containing 36 grams glacial acid per liter, stirring. Throw on double-pleated filter, reject until clear, evaporate 50 cc., and dry.

To another portion of 100 cc. repeat the foregoing, except that 20 cc. of lead acetate solution shall be used.

Residue from first treatment shall be multiplied by 1.2, and that from the second by 1.3, to bring back to the original 100 cc. of solution. Add to the corrected first residue the difference between corrected first and second residues, and calculate as soluble solids. This corrects for the dilution and removal by the lead salt.

Hide Powder

Events of the past summer have emphasized the necessity that hide powder possess the qualifications specified by the method. The principal importer of Vienna powder has supplied the referee with samples from four different lots of powder, none of which approach the standard of insolubility and absorption power. The Vienna powder, generally used because of its close adherence to the limits of insolubility and absorption, has recently shown such wide departure as to fall wholly without the range of allowable variation.

Inasmuch as the determination of tannin is dependent upon the character of the powder employed, no analysis can be truthfully reported as by the official method unless the powder employed shall fall within the prescribed limits. This distinction between powders within and without these limits is not only essential but vital to the value of results, from either the scientific or commercial standpoint. Many of the largest consumers of tanning materials base heavy contracts as to quality upon the official method, and unless it shall be closely stipulated that the powder employed shall answer the requirements of the method, something worse than controversy may result.

The referee, therefore, recommends that to Section VIII, page 80, shall be added the following paragraph:

"(*c*) Any analysis made with a powder which does not fulfil the conditions of the preceding paragraphs, shall not be reported as by this method."

The referee has made several experiments with powders falling without the requirements of the method, with results emphasizing the necessity for the foregoing recommendation.

Acid Hide Powders

The four powders considered in the following table were markedly acid, and when suspended in water preparatory to an analysis softened into a jelly-like mass which resisted the drying action of squeezing in linen. In order to remove the acidity of the powder it was necessary to use considerable quantities of sodium carbonate in the washing water:

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DETERMINATION OF NON-TANNINS USING ACID HIDE POWDERS

Methods	Nontannins Per cent.
Powder I :	
Without carbonate	16.93
With carbonate, washed three times	16.34
With carbonate, official	16.23
Powder II :	
Official	17.89
With carbonate, official	17.05
Powder III :	
Without carbonate, official	18.31
With carbonate, official	17.12
Powder IV :	
Without carbonate, official	17.68
With carbonate, official	16,74

When it is necessary to resort to an expedient, such as delicate neutralization, it is likely that different operators would return widely ranging results.

WASHING THE POWDER

A good powder was used and washed with the following results:

EFFECT OF VARIATIONS IN WASHING ON THE AMOUNT OF NON-TANNINS OBTAINED

Number of washings	Nontannins Per cent.
Not washed	19.74
Washed once in shaker	17.90
Washed twice in shaker	18.04
Washed three times in shaker	17.96
Washed four times in shaker	17.98

VARYING QUANTITIES OF HIDE POWDER

A large quantity of powder was washed and pressed and duplicate determinations made with increasing quantities of wet pressed hide, which contained 75 per cent. of moisture:

DETERMINATION OF NON-TANNINS WITH INCREASING QUANTITIES OF HIDE POWDER

Amount of hide powder	Nontannins Per cent.	Mean
50 grams wet hide	17.33 17.34	17.34
60 grams wet hide	16.61 16.63	16.62
70 grams wet hide	16.11 15.96	16.04

Inasmuch as the moisture content of the wet pressed hide is variable with the physical condition thereof, a definite statement of the dry hide present in the wet pressed cake must be made. Results are concordant for

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any definite quantity, but the fineness of some powders permits great loss in squeezing, and the actual dry hide present in the solution thereby becomes variable. The referee thinks it wise to stipulate that the dry hide present in the wet cake taken for the determination shall fall between 12 and 13 grams.

Volume of Solutions for Drying

Owing to the sensitiveness of tanning materials to the heat employed in drying, it is believed that the use of volumes yielding residues of from 400 to 500 milligrams is preferable to volumes giving greater residues. It is believed that if, instead of 100 cc. 50 cc. shall be used for total and soluble solids the resultant residue may be dried to constant weight in less time and at less risk of decomposition or oxidation. The experience of the referee is that residues of 400 milligrams may be dried to nearly constant weight on the steam or water bath in five hours, passing through an air or water oven for a half hour to remove surface moisture. While some laboratories are equipped to use volumes of 100 cc., others are not and it is believed that the smaller volume and residue will be advantageous in bringing the entire determination within one working day.

The referee would recommend, therefore, the substitution of 50 cc. wherever in the method 100 cc. is stipulated for drying.

Summary of Analyses

Oakwood Extract

Analyst	Total solids Per cent.	Soluble solids Per cent.	Insoluble Per cent.	Tannin Per cent.	Nontannin. Per cent.
1	43.45	42.24	1.21	25.64	16.60
2	43.37	42.54	0.83	25.78	16.76
3	42.74	42.13	0.61	25.20	16.93
4	42.53	40.65	1.88	24.72	15.93
5	42.85	42.22	0.63	24.07	18.15
6	43.23	42 53	0.70	25.07	17.46
7	42.94	42.29	0.65	25.25	17.01
8	43.29	42.26	1.03	25.11	17.15
Averages.	43.05	42.11	0.94	25.11	16.99
Maxima..	43.45	42.54	1.88	25.78	18.15
Minima .	42.53	40.65	0.61	24.07	15.93

Quebracho Extract

1	87.33	74.00	13.33	64.70	9.30
2	86.71	74.52	12.19	65.56	8.96
3	87.08	76.33	10.75	66.84	9.49
4	90.13	79.82	10.31	——	——
5	87.45	75.80	11.65	67.08	8.72
6	87.40	76.29	11.11	68.35	7.94
7	85.98	75.10	10.88	67.47	7.63
8	86.45	74.45	12.00	66.25	8.20
Averages.	87.32	75.70	11.59	66.61	8.61
Maxima..	90.13	79.82	13.33	67.47	9.49
Minima .	85.98	74.00	10.31	64.70	7.63

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The above eight analyses exhibit some improvement over the results previously obtained by collaboration. The quebracho is a severe trial on the accuracy of the method, owing to the high tannin and the extreme fineness of the insolubles in the analysis solution. Variations in non-tannins may be largely attributed to variations in character of hide powder used, as the analysts used the powder employed in their respective laboratories. Given a soluble solids determination accurate to 1 per cent. on a solid extract, it is likely that the principles of the non-tannin determination as now laid down in the method may be considered satisfactory. The range from maximum to minimum is relatively greater for all determinations, except non-tannins, in the oakwood than in the quebracho.

The Method

The following modifications of the official method, Bulletin 46, revised, page 79, VIII, Methods for the Analysis of Tanning Materials, are recommended:

III. Moisture. (*b*) 2. Read "For eight hours at 100° to 110° in an air bath."

IV. Total Solids. For "100 cc." read "50 cc."

V. Soluble Solids. For "double-folded filter" read "double-pleated filter." For "100 cc." read "50 cc.". For "kaolin" read "barytes".

Add paragraph giving optional method, as follows:

Optional Method

(*a*) To 100 cc. of the solution add 10 cc. of a solution of lead acetate (4 grams per liter), adding the reagent drop by drop from a burette and stirring meanwhile. Add 10 cc. of a solution of acetic acid (36 grams glacial acid per liter), stirring. Throw on double-pleated filter, reject until clear, and evaporate and dry 50 cc.

(*b*) On another portion of 100 cc. repeat the foregoing, except that 20 cc. of lead acetate solution shall be used.

Residue from (*a*) shall be multiplied by 1.2, and from (*b*) by 1.3, to bring back to the original 100 cc. Add to the corrected weight of the residue from (*a*) the difference between (*a*) and (*b*) and calculate the found residue to soluble solids. This corrects for dilution and removal by lead.

VI. Non-tannins. For lines 6-9 substitute the following: "Weigh the remaining three-quarters, which must contain between 12 and 13 grams of dry hide; add to 200 cc. of the solution and shake ten minutes. Throw on funnel with cotton plug in stem. return until clear, evaporate 50 cc. and dry."

VIII. Testing Hide Powder. (*a*) For "100 cc." read "50 cc.," and for "10 mg." read "5 mg.". (*b*) For "100 cc." read "50 cc.".

Add paragraph (*c*), as follows:

(*c*) Any analysis made with a powder which does not fulfill the conditions of the preceding paragraphs shall not be reported as by this method.

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REPORT ON COMPARATIVE HIDE-POWDER TESTS.

By William H. Krug.

Bulletin No. 62, U. S. Dept. of Agric.

During the last year various chemists engaged in the analysis of tanning materials have frequently complained of the character of the hide powder they were using, and have ascribed unsatisfactory results to variations in its absorbent power. The hide powder generally used in this country is made by the Vienna Experiment Station, and has, until recently, given almost universal satisfaction. Within the last year, however, it has undergone marked changes in that it is quite acid in reaction and retains a large amount of moisture after being squeezed even when repeatedly washed with water. When neutralized with sodium carbonate it loses this power of retaining water, but also decreases in its power of absorption with reference to tannin. It is generally claimed that this acid hide powder when used without previous neutralization gives a figure for non-tannins which is too low, and thus in turn results in too high a tanning value being ascribed to the material under examination.

It being evident that this matter is of great importance to all chemists interested in this branch of analytical chemistry, I some time ago sent a sample of quebracho extract, which had been ground and carefully mixed so as to render it strictly uniform in composition, to Mr. Alsop, of the United States Leather Company, and Mr. Teas, of the Elk Tanning Company. The sample was accompanied by a sufficient quantity of Vienna hide powder to make several determinations, and I suggested that the extract be analyzed both with and without previous neutralization of the powder with sodium carbonate. Unfortunately Mr. Teas was unable, through pressure of other work, to make more than one analysis in which he used the hide powder on hand at his laboratory. As this was derived from the same source as that sent by me for the comparative work, the two powders are probably identical. Mr. Alsop sent quite a complete report embodying results obtained both with hide powder in use at his laboratory and that sent him. The results are contained in the following table:

Mr. Alsop describes the method of washing the hide powder in use in his laboratory as follows:

Enough hide to make the determination is treated with about one hundred times its weight of water. If too acid to squeeze well, one-third the amount of sodium carbonate necessary to neutralize is added. It is then squeezed by hand through linen, treated with the same amount of water, and squeezed once more. If sodium carbonate has been added this washing is repeated again. It is then squeezed in a press and 50 grams taken for non-tannins. A portion is dried for determination of moisture. I can obtain more uniform results by this method than by the official method where 20 grams are taken for each determination.

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COMPARATIVE ANALYSES OF QUEBRACHO EXTRACT BOTH WITH AND WITHOUT PREVIOUS NEUTRALIZATION OF HIDE POWDER.

No.	Analyst	Method employed	Total solids Per ct.	Soluble solids Per ct.	Reds Per ct.	Non-tannins Per ct.	Tannins Per ct.	Remarks
1	Alsop	Laboratory hide, official method, not neutralized.	85.68	76.74	8.94	10.25	66.49	Showed traces of tannin in non-tannin filtrate. Filtrate was clear.
2	"	Laboratory hide, official method, neutralized.	85.68	76.74	8.94	12.74	64.00	Filtrate was turbid.
3	"	Laboratory hide, official method, treated with one third the amount of Na_2CO_3 necessary to neutralize.	85.68	76.74	8.94	9.78	66.96	Filtrate was clear and contained no tannin.
4	"	Hide powder sent for compaiative test, not neutralized.	85.68	76.74	8.94	10.68	66.06	Hide powder washed according to official method.
5	"	Hide powder sent for comparative test, treated with one-third the amount of Na_2CO_3 necessary to neutralize.	85 68	76.74	8.94	10.79	65.95	Hide powder washed according to official method.
6	"	Laboratory hide, not neutralized.	85.68	76.74	8.94	10.45	66.29	In these analyses the hide powder was washed according to the method adopted by Mr. Alsop's laboratory.
7	"	Laboratory hide, treated with one-third the amount of Na_2CO_3 necessary to neutralize.	85.68	76.74	8.94	9.90	66 84	
8	"	Laboratory hide, neutralized.	85.68	76.74	8.94	12.14	64.60	

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COMPARATIVE ANALYSES OF QUEBRACHO EXTRACT BOTH WITH AND WITHOUT PREVIOUS NEUTRALIZATION OF HIDE POWDER—(*Continued*).

No.	Analyst	Method employed	Total solids Per ct.	Soluble solids Per ct.	Reds Per ct.	Non-tannins Per ct.	Tannins Per ct.	Remarks
9	Teas	Laboratory hide.	84.95	75.05	9.90	10.65	64.40	Treatment of hide powder not stated.
10	Krug	Hide powder sent for comparative test, not neutralized.	85.35	77.43	7.92	10.08	67.35	20 grams hide powder used, washed according to official method.
11	"	Hide powder sent for comparative test, neutralized.	85.35	77.43	7.92	11.74	65.69	20 grams hide powder used. washed in a beaker ten times by decantation. using a liter of water each time. Nontannin filtrate showed traces of tannin and was turbid.
12	Krug	Hide powder sent for comparative test. neutralized.	85.35	77.43	7.92	10.49	66.94	30 grams of hide powder used, washed in a beaker ten times by decantation, using a liter of water each time. Nontaunin filtrate showed traces of tannin and was turbid.
13	"	Hide powder sent for comparative test, neutralized.	85.35	77.43	7.92	9.81	67.62	40 grams of hide powder used, washed in a beaker ten times by decantation, using a liter of water each time. Nontannin filtrate was clear and showed no tannin.

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A comparison of the results obtained by Mr. Alsop and myself shows a close concordance with reference to the non-tannins when the hide powder was not neutralized, and this is true both of the hide powder sent him for the comparative work and that in use in his own laboratory. When the acidity of the hide powder is neutralized, however, its absorption power becomes less, the non-tannin filtrates are turbid, and show traces of tannin. It was found that after neutralization it requires at least 40 grams of hide powder to obtain a filtrate free from tannin. The use of such a quantity is out of the question on account of the cost of the material.

The results clearly show the influence which the acidity of the hide powder exercises on the percentage of non-tannins obtained and render it evident that something should be done to enable chemists to obtain a neutral powder. While Mr. Alsop's method of treating with one-third the amount of sodium carbonate necessary for neutralization may be good, the question nevertheless arises if this is not merely choosing a mean between two evils. The accuracy of the official method depends to a very great extent on the character of the hide powder used, and every precaution should be employed to avoid sources of error in this feature of the method. I would therefore suggest that the matter be taken up by the association, possibly by inserting a clause in the present method, directing that the hide powder used in the determination of the non-tannins shall be neutral. The method as it now stands specifies certain standards as to the maximum amount of soluble matter which shall be present and the absorption power. It appears, however, that these restrictions do not cover fully the exigencies of the case.

A COMPARISON OF THE INTERNATIONAL FILTER-TUBE METHOD AND THE OFFICIAL HIDE-POWDER METHOD.

By H. W. Wiley and William H. Krug.

Bulletin No. 62, U. S. Dept of Agric.

The filter-tube method has been employed for many years by chemists on the continent in the analysis of tanning materials. It was officially adopted by the International Association of Leather Trade Chemists at a conference held in England in 1897, and has since been retained by that association. The objection made by American chemists to this method is that it yields a figure for non-tannins which is too low, and thus gives the tanning material a higher value than it should have. At the last meeting of the international association, which was held in Paris last summer, and which one of us attended as American delegate, it was arranged with Professor Procter to make a series of comparative tests on tanning materials which were to be furnished by him. These materials comprised a sample each of oak-wood extract, chestnut-wood extract, liquid quebracho extract, mimosa extract, solid quebracho extract, sumac, valonia, golden wattle, and mimosa bark. Upon arrival of the samples it was found that

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the bottle containing the liquid quebracho extract was broken, and the analyses of the sumac and golden wattle were interrupted by the breaking of the bottles during extraction. The analyses by the filter-tube method were made in Professor Procter's laboratory, while those by the official method were made in the Division of Chemistry, United States Department of Agriculture. The results obtained are compiled in the following tables:

COMPARISON OF RESULTS OBTAINED BY THE OFFICIAL AND THE FILTER-TUBE METHODS IN THE ANALYSIS OF TANNING MATERIALS

	Oak-wood extract		Chestnut-wood extract		Mimosa extract		Solid quebracho extract	
Constituents	Filter-tube method Per ct.	Official method Per ct.	Filter tube method Per ct.	Official method Per ct.	Filt r tube method Per ct.	Official method Per ct.	Filter tube method Per ct.	Official method Per ct.
Moisture	59.60	59.50	59.89	60.36	50.80	50.28		16.84
Total solids by dilution	—	40.34	—	39.74	—	49.90	81.10	83.39
Soluble solids by dilution	—	40.02	—	38.89	—	49.70	69.10	75.20
Reds	0.40	0.32	0.80	0.85	0.00	0.20	12.00	8.19
Nontannins	13.00	14.66	10.60	13.11	9.00	12.33	—	14.01
Available tannins	27.00	25.36	28.80	25.78	40 20	37.37	—	61.19

	Valonia		Mimosa bark	
Constituents	Filter-tube method Per ct.	Official method Per ct.	Filter-tube method Per ct.	Official method Per ct.
Moisture	12.20	12.60	10.80	—
Total solids in extract[1]	—	53.51	—	47.04
Soluble solids in extract[1]	—	52.69	—	43.30
Reds in extract[1]	—	0.82	—	3.74
Nontannins	12.90	13.20	10.70	10.11
Available tannins	40.30	39.49	32.30	33.19
Total insoluble matter	34.60	34.71	46.20	—

[1] Calculated to original material.

The results show in general a very good agreement as to the amount of moisture present in the samples. The same is true of the reds, except with the solid quebracho extract, where the high percentage obtained with the filter-tube method shows the effect of rapid cooling of the diluted extract, as specified by this method, upon the sensitive tannin which it contains. The chief point of interest in these figures is naturally the non-tannins, as these indicate the variation caused by the different application of the hide powder. In every case except one, that being mimosa bark, the filter-tube method gives lower non-tannins than the official method and

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correspondingly higher tannins. It is evident, therefore, that a true international method is an absolute necessity. Large quantities of tanning materials are annually sold to American importers, the European merchant demanding payment on the basis of the results obtained by the filter-tube method. The American importer in turn is forced to sell to the tanner on the basis of figures obtained by the official method, the result being constant friction between buyer and seller. It gives us pleasure to state that the first step toward a uniform method has been taken, the International Association at its last conference in Paris having adopted the method of cooling the diluted extracts used in this country. It is to be hoped that the efforts in this direction will be continued, and will result finally in the development and universal adoption of a truly international method for the analysis of tanning materials.

Mr. Sawyer gave a very interesting talk on various debatable points in the present method for the analysis of tanning materials. He advocated the use of a smaller volume of the solutions in determining total and soluble solids, and suggested a series of comparative experiments on various methods of filtration.

MR. WILEY: I attended the International Congress of Leather Chemists, which met in Paris in August, 1900. The president of this congress, Prof. H. R. Procter, is well known to chemists in this country, especially those engaged in the tanning industries.

I was most cordially received as the representative of the Association of Official Agricultural Chemists and invited to a seat of honor at the president's right, and asked to take part in the discussion. Finding that there was no American representative in the congress. I decided to become a member thereof, in order that we might be not only officially but actively represented. The proceedings of the congress were conducted in three languages, which made the sessions rather monotonous. Each member of the congress spoke in his native language, and his speech was afterwards repeated in the other two languages of the congress, French, German, and English being the three languages recognized.

In adopting methods of research and analysis the processes recommended by the Association of Official Agricultural Chemists received due consideration. In fact, an earnest effort was made to harmonize the methods employed on the Continent with those employed by our own chemists. Some of our methods were adopted en bloc and others in a more or less modified form. It is evident that with a very little effort we may be able to unify the methods in vogue both in America and in Europe. This would be extremely useful, not only from a scientific point of view, but especially from the commercial aspect, since in this case analyses made by chemists on the two continents would be conducted by the same methods and be strictly comparable.

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REPORT ON TANNIN.

By W. K. Alsop, Referee.

Bulletin No. 67, U. S. Dept. Agric.

The referee sent samples of chestnut extract, solid quebracho extract, Vienna hide powder (Marked No. 1), and dry chromed hide powder (marked No. 2), to fifteen chemists, requesting that analyses be made by the official method, and also after the following directions:

Quantity of Material

Use such quantity as will give 0.35 to 0.45 gram tanning material per 100 cc. Dissolve as in official method.

Non-tannins

(1) Prepare 20 grams of hide powder (No. 1) by digesting three days with 500 cc. water, adding on each day 0.2 gram of chrome alum in solution. Wash by squeezing through linen, continue washing until no precipitate is obtained in wash water with barium chloride. Squeeze hide in press and proceed exactly as in official method.

(2) To 14 grams of dry chromed hide powder (No. 2) in a shaker glass add 200 cc. of the tanning solution; let stand two hours, stirring frequently. Shake on shaker 15 minutes, throw on funnel with cotton plug in stem; evaporate 50 cc.

Determinations were requested on both dilutions of the extracts with wet chromed hide, and on the weaker solution by dry chromed hide.

Mr. Geo. P. Craighill last spring called the referee's attention to a method of analysis involving the use of chromed hide powder. He is using it in his laboratory with very satisfactory results. It is based on the method proposed by Mr. B. Weiss, of Vienna. As stated in an article in the *Leather Trades Review*, the essential details of his method are as follows:

To every 100 grams hide in 2 liters of water are added 3 grams chrome alum in solution, this alum solution being added in equal parts on three successive days. The hide is then washed until free from sulphates. To the last wash water some formalin is added. The hide is then pressed slightly and kept in a damp chamber.

Mr. Weiss states that he has kept it in that manner as long as two months, without decomposition or other change.

The non-tannin determination is carried out as follows: To 130 cc. of tanning solution (0.6 to 0.8 gram solids per 100 cc.) add an equivalent of 7 grams dry hide, stir frequently, let stand overnight, squeeze through muslin filter, and evaporate 100 cc.

Mr. Craighill modifies the method as follows: After chroming he keeps the hide in water to which some formalin has been added, squeezing enough hide for each determination, then he proceeds as in the official method, using shaker. He also states that he has kept hide some time in water with formalin in it without any change, but that he found hide deteriorated when kept as described by Mr. Weiss.

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TABLE 1.—CHESTNUT EXTRACT—OFFICIAL METHOD (0.8 GRAM PER 100 CC.).

Analyst	Moisture Per cent.	Total solids Per cent.	Soluble solids Per cent	Reds Per cent.	Non-tannins Per cent.	Tannins Per cent.	Hide powder	Weight of wet hide used Grams	Water in wet hide Per cent.	Weight of dry hide Grams	Method of drying
G. P. Craighill.....	53.69	46.48	44.68	1.80	15.86	28.82	No. 1, official.....	40.00	65.4	13.84	8 hours, 100° air bath
					15.19	29.49	No. 1, chromed.....	38.00	64.4	13.53	"
					14.76	29.92	No. 2, dry chromed..	—	—	14 00	"
H. T. Wilson	54.32	46.00	44.13	1.87	15.50	28.63	No. 1, official.....	36.00	64.68	12.70	"
					14.13	30.00	No. 1, chromed.....	44.20	71.92	12.40	"
					15.09	29.04	Laboratory, official..	44.40	73.16	11.90	"
					13.38	30.75	Laboratory, chromed	42.00	68.45	13 25	"
H. C. Reed	54.11	45.58	44.79	0.79	14.58	30.21	No. 1, official.....	40.40	68.60	12.68	8 hours, 105° air bath
					14.02	30.77	No. 1, chromed.....	37.54	66.30	12.65	"
					14.07	30.72	Laboratory, chromed	34.44	65.70	11.81	"
F. P. Veitch.....	54.51	45.36	44.39	0.97	15.02	28.37	No. 1, official.....	70.00	80.60	13.58	4 to 7 hours, 70° in vacuo
W. H. Krug.....	54.70	46.34	44.83	1.51	14.44	30.39	"	—	—	—	10 hours, 70° in vacuo
					15.61	29.22	Laboratory, official..	—	—	—	"
					14.10	30.73	Laboratory, chromed	—	—	—	"
F. H. Yocum.....	—	46.08	45.57	0.51	15.39	30.18	No. 1, official.....	50.00	76.4	11.80	24 hours, 96° steam oven
					14.13	31.44	No. 1, chromed.....	50.00	71.7	14.15	"
F. H. Small	54.53	45.56	44.76	0.80	14.65	30.11	No. 1, official.....	45.50	72.9	12.33	"
					14.03	30.73	No. 1, chromed.....	45.20	73.4	12.02	"
J. N. Hurty.....	53.19	46.77	45.70	1.07	16.77	28.93	No. 1, official.....	51.92	75.71	12.61	8 hours, 110°
					15.90	29.80	No. 1, chromed.....	58.85	81.28	11.02	"
W. H. Teas.....	—	45.94	45.17	0.77	14.00	31.17	No. 1, official.....	50.00	70.00	15.00	18 hrs., 96° hot-water oven
					13.30	31.87	No. 1, chromed.....	50.00	79.00	10.50	"
Kerr and Mosbaugh..	—	48.04	44.42	3.62	15.71	28.71	No. 1, official.....	—	—	—	
M. S. McDowell	—	46.60	44.10	2.50	14.88	29.22	"	49.50	—	—	24 hours, hot-water oven

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C. H. Brown	—	45.33	44.00	1.33	14.28	29.72	No. 1, official	64.00	80.40	12.54	24 hrs., 96° hot-water oven
					14.06	29.94	No. 1, chromed	55.00	77.50	12.38	"
					14.11	29.89	No. 2, dry chromed ..	—	—	14.00	"
W. K. Alsop	—	45.66	44.22	1.44	14.58	29.64	No. 1, official	64.00	80.50	12.48	"
					14.41	29.81	No. 1, chromed	55.00	75.80	13.31	"
Average	—	46.13	44.67	1.46	15.05	29.62	No. 1, official	—	—	—	
					14.35	30.32	No. 1, chromed	—	—	—	
Highest	—	48.04	45.70	3.62	16.77	31.17	No. 1, official	—	—	—	
					15.90	31.87	No. 1, chromed	—	—	—	
Lowest	—	45.33	44.00	0.51	14.00	28.37	No. 1, official	—	—	—	
					13.30	29.49	No. 1, chromed	—	—	—	
Greatest difference	—	2.71	1.70	3.11	2.77	2.80	No. 1, official	—	—	—	
					2.60	2.38	No. 1, chromed	—	—	—	
Greatest difference from average.	—	2.38	1.03	2.16	1.72	1.55	No. 1, official	—	—	—	
					1.55	1.55	No. 1, chromed	—	—	—	

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TABLE 2.—CHESTNUT EXTRACT—EXPERIMENTAL METHOD (0.35 TO 0.45 GRAM TANNING MATERIAL PER 100 CC.).

Analyst	Moisture Per cent.	Total solids Per cent.	Soluble solids Per cent.	Reds Per cent.	Non-tannins Per cent.	Tannins Per cent.	Hide powder	Weight of wet hide used Grams	Water in wet hide Per cent.	Weight of dry hide Grams	Method of drying
G. P. Craighill.....	53.69	46.26	44.22	2.04	15.42	28.80	No. 1, official.....	40.00	68.4	12.64	8 hours, 100° air bath
					14.52	29.70	No. 1, chromed.....	36.00	64.4	12.82	"
					14.50	29.72	No. 2, dry chromed ..	—	—	14.00	"
H. T. Wilson	54.32	45.63	44.34	1.29	15.51	28.83	No. 1, official.....	36.55	64.46	12.99	"
					14.40	29.94	No. 1, chromed.....	41.00	69.85	12.36	"
					13.99	30.35	No. 2, dry chromed ..	—	—	*7.00	"
					14.08	30.26	"	—	—	*7.00	"
					14.33	30.01	No. 3, laboratory, official	48.00	72.31	13.29	"
					13.63	30.71	Laboratory, chromed.	40.00	68.45	12.62	"
H. C. Reed.....	54.11	45.75	44.95	0.80	14.25	30.70	Laboratory, official..	45.90	2.2	12.76	8 hours, 105° air bath
					13.97	30.98	No. 1, chromed.....	38.33	69.1	11.85	"
					14.00	30.95	No. 2, dry chromed ..	—	—	14.00	"
F. P. Veitch.....	54.51	45.59	44.83	0.78	15.27	29.56	No. 1, official.....	70.00	80.6	13.58	4 to 7 hours, 70° in vacuo
					15.72	29.11	No. 2, dry chromed ..	—	—	14.00	"
F. H. Small	54.77	45.52	44.41	1.11	14.35	30.06	No. 1, official..	45.4	72.9	12.30	24 hours, 96° steam bath
					14.12	30.29	Laboratory, official ..	50.0	78.8	10.60	"
					14.01	30.40	No. 1, chromed.....	44.7	73.4	11.89	"
					14.03	30.38	Laboratory, chromed.	45.0	75.0	11.25	"
					14.92	29.49	No. 2, dry chromed ..	—	—	14.00	"
F. H. Yocum.....	52.96	47.04	46.41	0.63	15.73	30.68	No. 1, official.....	—	76.4	—	"
					14.52	31.89	No. 1, chromed.....	—	71.7	—	"
M. S. McDowell.....	—	46.13	44.07	2.06	13.38	30.69	No. 1, official.....	51.0	—	—	24 hours, hot-water oven
					14.37	29.70	No. 1, chromed.....	50.0	—	—	"
W. H. Teas.....	—	46.00	44.86	1.14	14.05	30.81	No. 1, official.....	50.0	70.0	15.00	18 hours, hot-water oven
					13.76	31.10	No. 1, chromed.....	50.0	79.0	10.50	"

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C. H. Brown.....	—	45.37	44.00	1.37	14.47	29.53	No. 1, official.....	64.0	80.40	12.54	24 hrs., 96° hot-water oven
					13.83	30.17	No. 1, chromed.....	55.0	77.5	12 38	"
					14.18	29.82	No. 2, dry chromed ..	—	—	14.00	"
W. K. Alsop.....	—	45.59	45.00	0.59	14.46	30.54	No. 1, official.....	64.0	80.50	12.48	"
					14.01	30.99	No. 1, chromed.....	55.0	75.80	13.31	"
					14.06	30.94	No. 2, dry chromed ..	—	—	14.00	"
Average	54.06	45.88	44.70	1.17	14.74	29.96	No. 1, official.....	—	—	—	
					14.15	30.55	No. 1, chromed.....	—	—	—	
					14.43	30.27	No. 2, dry chromed ..	—	—	—	
Highest	—	47.04	46.41	2.06	15.73	30.81	No. 1, official.....	—	—	—	
					14.52	31.89	No. 1, chromed.....	—	—	—	
					15.72	30.95	No. 2, dry chromed ..	—	—	—	
Lowest	—	45.37	44.00	0.59	13.38	28.80	No. 1, official.....	—	—	—	
					13.76	29.70	No. 1, chromed.....	—	—	—	
					13.99	29.11	No. 2, dry chromed ..	—	—	—	
Greatest difference.	—	1.67	2.41	1.47	2.35	2.01	No. 1, official.....	—	—	—	
					0.76	2.19	No. 1, chromed.....	—	—	—	
					1.74	1.84	No. 2, dry chromed ..	—	—	—	
Greatest difference from average	—	1.16	1.71	0.89	1.36	1.16	No. 1, official.....	—	—	—	
					0.39	1.34	No. 1, chromed.....	—	—	—	
					1.29	1.18	No. 2, dry chromed ..	—	—	—	

* 100 cc. of solution used.

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TABLE 3.—QUEBRACHO EXTRACT—OFFICIAL METHOD (0.8 GRAM SOLIDS PER 100 CC.).

Analyst	Moisture Per cent.	Total solids Per cent.	Soluble solids Per cent.	Reds Per cent.	Non-tannins Per cent.	Tannins Per cent.	Hide powder	Weight of wet hide used Grams	Water in wet hide Per cent.	Weight of dry hide Grams	Method of drying	Used in filtering soluble solids
G. P. Craighill	13.72	86.37	77.52	8.85	9.23	68.29	No. 1, official	40.00	65.40	13.84	8 hrs, 100° air bath	No kaolin
					8.43	69.09	No. 1, chromed	38.00	64.40	13.53	"	
					8.38	69.14	No. 2, dry chromed	—	—	14.00	"	
H. T. Wilson	16.52	82.60	74.93	7.67	9.82	65.11	No. 1, official	46.00	68.48	14.50	"	Barytes
					8.94	65.99	No. 1, chromed	44.00	74.59	11.17	"	
					9.04	65.89	Laboratory, official	45.00	66.05	15.27	"	
					8.90	66.03	Laboratory, chromed	45.00	66.46	15.09	"	
H. C. Reed	14.97	84.75	74.95	9.80	8.26	66.69	No. 1, official	41.13	70.20	12.30	8 hrs., 105° air bath	10 grams kaolin
					7.91	67.04	No. 1, chromed	39.17	67.20	12.84	"	
					8.47	66.48	Laboratory, chromed	34.84	67.20	11.42		
F. P. Veitch	16.17	83.64	75.62	8.02	9.17	66.45	No. 1, official	70.00	80.60	13.58	4 to 7 hours, 70° in vacuo	
F. H. Small	16.38	83.85	73.80	10.05	8.43	65.37	"	47.20	72.90	12.79	24 hrs., 96° in steam oven	Kaolin
					7.98	65.82	No. 1, chromed	49.50	73.40	13.17	"	
W. H. Krug	16.20	85.00	76.22	8.78	7.90	68.32	No. 1, official	—	—	—	10 hrs., 70° in vacuo	
					9.51	66.71	Laboratory, official	—	—	—	"	
					9.54	66.68	Laboratory, chromed	—	—	—	"	
F. H. Yocum	14.22	85.78	75.42	10.36	9.88	65.54	No. 1, official	50.00	76.40	11.80	24 hrs., 96° steam oven	Kaolin
					8.87	66.55	No. 1, chromed	50.00	71.70	14.15	"	
J. N. Hurty	15.67	84.16	74.06	10.10	10.81	63.25	No. 1, official	54.91	77.00	12.63	8 hours, 110°	
					10.83	63.23	No. 1, chromed	54.74	81.28	10.28	"	

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Kerr and Mosbaugh	14.22	85.78	71.26	14.52	10.08	61.18	No. 1, official.....	—	—	—		
M. S. McDowell	—	84.32	77.37	6.95	9.65	67.72	"	51.00	—	—	24 hours, hot-water oven	No kaolin
W. H. Teas....	—	85.43	73.12	12.31	8.57	64.55	"	50.00	70.00	15.00	18 hours, hot-water oven	Kaolin
					7.83	65.29	No. 1, chromed...	50.00	79.00	10.50	"	
					7.99	65.13	Laboratory, chromed	50.00	78.50	10.75	"	
C. H. Brown...	14.92	84.60	73.24	11.36	8.72	64.48	No. 1, official.....	64.00	80.40	12.54	24 hours, 96° hot-water oven	10 grams kaolin
					8.27	64.97	No. 1, chromed...	55.00	77.50	12.38	"	
W. K. Alsop...	14.87	84.84	74.48	10.36	9.44	65.04	No. 1, official.....	64.00	80.50	12.48	"	10 grams kaolin
					8.86	65.62	No. 1, chromed...	55.00	75.80	13.31	"	
Average.....	—	84.70	74.77	9.93	9.23	65.54	No. 1, official ...	—	—	—		
					8.66	66.13	No. 1, chromed...	—	—	—		
Highest	—	86.37	77.52	14.52	10.81	68.32	No. 1, official.....	—	—	—		
					10.83	69.09	No. 1, chromed ..	—	—	—		
Lowest	—	82.60	71.26	6.95	8.26	61.18	No. 1, official.....	—	—	—		
					7.83	63.23	No. 1, chromed...	—	—	—		
Greatest difference	—	3.77	6.26	7.57	2.55	7.14	No. 1, official.....	—	—	—		
					3.00	5.86	No. 1, chromed...	—	—	—		
Greatest difference from average	—	2.10	3.51	4.59	1.58	4.36	No. 1, official.....	—	—	—		
					1.97	2.96	No. 1, chromed...	—	—	—		

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TABLE 4.—QUEBRACHO EXTRACT—EXPERIMENTAL METHOD (0.35 TO 0.45 GRAM TANNING MATERIAL PER 100 CC.).

Analyst	Moisture Per cent.	Total solids Per cent.	Soluble solids Per cent.	Reds Per cent.	Non-tannins Per cent.	Tannins Per cent.	Hide powder	Weight of wet hide used Grams	Water in wet hide Per cent.	Weight of dry hide Grams	Method of drying	Used in filtering soluble solids
G. P. Craighill	13.72	86.45	77.26	9.19	9.09	68.17	No. 1, official	40.00	68.4	12.64	8 hrs., 100° air bath	No kaolin
					8.27	68.99	No. 1, chromed	36.00	64.4	12.81	"	
					8.34	68.92	No. 2, dry chromed	—	—	14.00	"	
H. T. Wilson	16.52	82.91	76.15	6.76	10.75	65.40	No. 1, official	46.00	67.96	14.73	"	Barytes
					8.51	67.64	No. 1, chromed	44.00	74.59	11.17	"	
					8.59	67.56	No. 2, dry chromed	—	—	*7.00	"	
					8.56	67.59	"	—	—	*7.00	"	
					9.11	67.04	Laboratory, official	45.00	66.34	15.14	"	
					8.34	67.81	Laboratory, chromed	45.00	66.46	15.09	"	
H. C. Reed	14.97	85.40	77.93	7.47	8.96	68.97	Laboratory, official	47.62	73.4	12.66	8 hrs., 105° air bath	5 grams kaolin
					8.39	69.54	No. 1, chromed	37.88	67.9	12.15	"	
					8.83	69.10	No. 2, dry chromed	—	—	14.00	"	
F. P. Veitch	16.17	83.71	77.92	5.79	9.63	68.29	No. 1, official	70.00	80.60	13.58	4 to 7 hrs. in vacuo, 70°	
					11.00	66.92	No. 2, dry chromed	—	—	14.00	———	
J. H. Yocum	13.90	86.10	75.90	10.20	9.94	65.96	No. 1, official	50.00	76.40	11.80	24 hrs. steam bath, 96°	Kaolin
					9.01	66.89	No. 1, chromed	50.00	71.70	14.15	"	
F. H. Small	16.45	84.21	76.15	8.06	8.73	67.42	No. 1, official	46.40	72.90	12.57	"	Kaolin
					8.31	67.84	No. 1, chromed	46.40	73.40	12.34	"	
					8.86	67.29	No. 2, dry chromed	—	—	14.00	"	
					8.56	67.59	Laboratory, official	50.70	78.80	12.08	"	
					8.92	67.23	Laboratory, chromed.	45.00	75.00	11.25	"	

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W. H. Teas....	—	85.50	74.07	11.43	9.09	64.98	No. 1, official.....	50.00	70.00	15.00	18 hours hot-water oven	Kaolin
	—	—	—	—	8.51	65.56	No. 1, chromed...	50.00	79.00	10.50	"	
		85.41	73.94	11.47	8.61	65.33	Laboratory, chromed.	50.00	78.50	10.75	"	
M. S. McDowell	—	85.34	—	—	9.72	—	No. 1, official.....	50.00	—	—	24 hours hot-water oven	
					9.00	—	No. 1, chromed...	50.00	—	—	"	
C. H. Brown...	14.92	83.88	74.77	9.11	9.23	65.54	No. 1, official.....	64.00	80.40	12.54	24 hours, 96° hot-water oven	10 grms. kaolin
					8.42	66.35	No. 1, chromed...	55.00	77.50	12.38	"	
					8.71	66.06	No. 2, dry chromed	—	—	14.00	"	
W. K. Alsop...	14.87	85.20	75.37	9.83	9.45	65.92	No. 1. official.....	64.00	80.50	12.48	"	10 grms. kaolin
					8.71	66.66	No. 1, chromed...	55.00	75.80	13.31	"	
					9.01	66.29	No. 2, dry chromed	—	—	14.00	"	
Average.....	—	84.76	75.95	8.81	9.51	66.46	No. 1, official.....	—	—	—		
					8.57	67.38	No. 1, chromed...	—	—	—		
					8.99	66.96	No. 2, dry chromed	—	—	—		
Highest	—	86.45	77.93	11.47	10.75	68.29	No. 1, official.....	—	—	—		
					9.01	69.54	No. 1, chromed...	—	—	—		
					11.00	69.10	No. 2, dry chromed	—	—	—		
Lowest	—	82.91	73.94	5.79	8.73	64.98	No. 1, official.....	—	—	—		
					8.27	65.56	No. 1, chromed...	—	—	—		
					8.34	66.06	No. 2, dry chromed	—	—	—		
Greatest difference.	—	3.54	3.99	5.68	2.02	3.31	No. 1, official.....	—	—	—		
					0.74	3.98	No. 1, chromed...	—	—	—		
					2.66	3.04	No. 2, dry chromed	—	—	—		
Greatest difference from average.	—	1.85	2.01	3.02	1.24	1.83	No. 1, official.....	—	—	—		
					0.44	2.16	No. 1, chromed...	—	—	—		
					2.01	2.14	No. 2, dry chromed	—	—	—		

* 100 cc. of solution used.

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Mr. Craighill further states that he has prepared a dry chromed hide powder that retains the power of absorbing tannin sufficiently for use in analyses. Mr. Weiss says that he was unable to prepare such a powder. Mr. Craighill proceeds as follows:

The washed chromed powder is lightly squeezed, then thoroughly broken up and washed with alcohol, squeezed, the washing repeated, squeezed again and carefully "woolled," so that no lumps are left, then it is washed in ether, squeezed by hand and again carefully "woolled." The drying is done at ordinary temperature. It is essential that the finished product be entirely free from hard lumps, which condition can only be secured by extreme care during the process.

The dry chromed powder sent out with the samples was furnished by Mr. Craighill. It appears to be essential that hide so prepared be digested some time in the tannin solution and then shaken vigorously. This powder is free from solubles and by its use the correction for water introduced with the wet hide is avoided and the method simplified.

The most important claims for chromed hide, either wet or dry, are, that the soluble substances in the hide are rendered insoluble, and either for that reason or some other, not explained, it causes hide powders to give concordant results that otherwise differ widely by the method now in use.

This is an established fact, and for that reason alone the referee considers that he is justified in urging that the use of chromed hide be made official. A summary of the results of the cooperative work on samples is given in the table.

These reports indicate—

(1) That the results obtained by the use of wet chromed hide powder are more accurate than those with unchromed hide. This is especially so in the results reported as obtained by the use of the weaker solution.

Several chemists did not report results with the dry chromed powder. Two reported that they could not get satisfactory results with it. The reports received are encouraging and indicate that the subject should be thoroughly investigated.

(2) That more concordant results can be obtained by the use of the weaker solution.

(3) That the method of drying has not much influence on the tannin result, provided the determinations in each analysis are dried in the same manner.

(4) That the determination of soluble solids is the weakest point in the method, and that some method must be adopted that chemists will follow.

Mr. Wilson reports as follows regarding the use of chromed hide powder.

Two things are well established. Powders unlike in absorptive power become alike when properly chromed. It is possible to produce a dry chromed powder ready for use. In support of the latter statement the referee has distributed a powder which yields results of astonishing con-

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cordance. The method for its preparation is very simple, and one which powder makers may easily adopt. In the opinion of the writer, the association should take official cognizance of this feature and recommend its adoption by powder producers.

Mr. Wilson reports in regard to "unlike powders being made alike," as follows:

TABLE 5.—QUEBRACHO EXTRACT.—(SOLUTION 0.35 TO 0.45 GRAM TANNIN PER 100 CC.).

*Various Hide Powders, Chromed and Unchromed.**

Hide powder	Volume solution shaken cc.	Wet hide Grams	Moisture Per cent.	Dry hide Grams	Dry hide per 100 cc. solution Grams	Nontannin Per cent.
I, unchromed	200	46	67.96	14.73	7.37	10.75
III, unchromed	200	45	66.54	15.14	7.57	9.11
I, chromed	200	44	74.59	11.17	5.59	8.51
III, chromed	200	45	66.46	15.09	7.55	8.34
IV, chromed	100	25	54.36	11.40	11.40	8.23
I, chromed	200	40	74.59	10.16	5.08	8.56
"	200	50	74.59	12.70	6.35	8.57
"	200	60	74.59	15.24	7.62	8.57
III, chromed	200	40	71.40	11.44	5.72	8.30
"	200	50	71.40	14.30	7.15	8.33
"	200	60	71.40	17.16	8.58	8.33
II, dry chromed	100	–	—	7.00	7.00	8.59
"	100	–	—	7.00	7.00	8.56
Average all chromed powders	—	—	—	—	—	8.44

* All dryings at 100° in air, eight hours.

Mr. Wilson further reports:

It may be mentioned that powder No. 4 was simply a piece of white hide from the tannery, dried, rasped, degreased with ether, and chromed in the usual way. It will be noticed in Table 5 that diverse powders, after chroming, not only furnish concordant results, but may be applied in various ways and various quantities without altering the results, a condition impossible with unchromed powder. The range from the average of all the chromed powders is only 0.21 per cent., or less than 2.5 per cent. of the whole percentage.

Mr. Wilson calls attention to that part of the table showing results obtained by him on hides Nos. I and III, when varying quantities of hide powders were used per 200 cc. of solution, and he states that "with progressively increasing hide, no decrease of non-tannin occurs."

Mr. Small reports some results obtained with a poor hide powder. He says:

These, although not obtained by the official method, may be of interest because the hide powder used is of exceptionally poor quality, it being impossible to get results of any value with it in the raw state.

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TABLE 6.—DETERMINATION OF NON-TANNINS (SMALL).

	Chestnut extract Non-tannins		Quebracho extract Non-tannins	
	Chromed Per cent.	Unchromed Per cent.	Chromed Per cent.	Unchromed Per cent.
Poor hide	13.68	17.38	7.89	11.84
Hide No. 1	14.01	14.35	8.31	*8.73

* Official Method

Mr. Reed reports some analyses made with his laboratory hide, and also a hide marked "B" in the table. The non-tannins only are tabulated.

TABLE 7.—DETERMINATION OF NON-TANNINS (REED).

	Unchromed		Chromed	
	B. Per cent.	Laboratory Per cent.	B. Per cent.	Laboratory Per cent.
A solid quebracho extract, 9½ grams per liter	14.50	13.24	12.45	12.21
A solid quebracho extract, 6 grams per liter	15.10	13.18	12.02	12.23
Chestnut extract, 17½ grams per liter	15.99	—	13.68	14.07
Chestnut extract, 13½ grams per liter	15.90	14.25	13.52	—
Chestnut oak bark extract	—	22.24	—	21.38

Mr. Reed states:

I am of the opinion that if hide powder B will answer the requirements, after being chromed pretty nearly any hide will do, for B is about as poor a hide powder as I have ever handled. That the chroming of B hide makes it fit for the analyses is abundantly proved by the result. The more analyses I make with chromed hide, the better I am pleased with the method.

Mr. Craighill has sent me results obtained with various powders unchromed, wet chromed and dry chromed. In the table following, A, B, and C are three different hide powders, the determinations being made on the same solution. Nos. 1 to 5 are results obtained on different extracts.

TABLE 8.—DETERMINATION OF NON-TANNINS (CRAIGHILL).

	Non-tannins		
	Unchromed Per cent.	Wet chromed Per cent.	Dry chromed Per cent.
A	20.35	19.48	—
B	24.24	19.52	—
C	22.57	19.63	—
1	20.44	18.89	18.84
		18.79	18.76
		18.77	18.84
2	17.61	16.73	16.74
3	17.73	16.52	16.76
4	17.68	16.76	16.71
5	16.75	—	15.54
			15.72
			15.70

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TABLE 8.—DETERMINATION OF NON-TANNINS (CRAIGHILL)—*Continued.*

Effect of Chroming One Day and Three Days.

	Non-tannins		
	Unchromed Per cent.	Wet chromed Per cent.	Dry chromed Per cent.
3 days	—	16.61	16.56
1 day	—	16.94	16.86

Mr. Yocum reports as follows on a sample of Freiberg hide powder. The dry-chromed hide was digested in the tannin solution overnight.

TABLE 9.—DETERMINATION OF NON-TANNINS WITH FREIBERG HIDE POWDER (YOCUM).

	Non-tannins		
	Unchromed Per cent.	Wet chromed Per cent.	Dry chromed Per cent.
Chestnut extract	—	14.81	15.02
Quebracho extract	12.15	8.93	9.01

With hide No. 1, wet chromed, Mr. Yocum's results were, with quebracho extract, 8.87; chestnut extract, 14.52.

Mr. Hurty reports the following experiments with dry-chromed hide, which was prepared as follows:

Fifty grams of hide were digested three days, with 3 grams of chrome alum in solution, 1 gram being added each day, washed free from sulphates, squeezed, digested twice with 98%, alcohol to remove water, then dried. In all trials the same extract was used. The tannin solution was 1 per cent., and 10 grams of hide were used with 150 cc. of solution, 50 cc. evaporated. Laboratory hide was used for filter and official methods. The figures are for non-tannins.

TABLE 10.—COMPARATIVE DETERMINATIONS OF NON-TANNINS BY THREE METHODS (HURTY).

Samples	Filter method Per cent.	Official method Per cent.	Dry chromed hide Per cent.
First set	16.1	17.38	16.76
	—	—	16.35
	—	—	16.60
Second set[1]	—	—	15.62
	—	—	15.66
	—	—	15.72
Third set[1]	—	—	15.52
	—	—	15.66
	--	—	15.18
Fourth set[2]	—	—	15.18
	—	—	15.10
	—	—	15.54

[1] Dry chromed hide prepared as above, except digested six days.

[2] Obtained with "formal hide."

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The "formal hide" was prepared as follows: Fifty grams of the hide was washed twice with distilled water, then treated for twelve hours with 10 cc. of 40 per cent. formaldehyde in 1,000 cc. of water, washed once, squeezed, and treated twice with alcohol.

Mr. Hurty used twice as much chrome alum as was used in the other experiments, reported. It is evident from his results that prolonged chroming with this amount of chrome tends to decrease the amount of non-tannins.

The referee submits the following results, obtained on six different samples of extract, in the course of routine work. Hide powder A is Vienna hide, and B is a powder that gives very unsatisfactory results with the official method when unchromed:

TABLE 11.—DETERMINATION OF NON-TANNINS (ALSOP).

	Hide	Unchromed Per cent.	Wet chromed Per cent.	Three grams chrome to 100 grams hide
1	A	16.34	14.87	Chromed 3 days
	B	18.72	14.77	"
2	A	16.25	15.06	Chromed 24 hours
	B	—	15.06	"
3	A	18.26	15.85	"
	B	--	16.10	"
4	A	16.76	15.79	Chromed 5 minutes on shaker
	B	19.31	15.89	"
5	A	16.54	15.59	"
	B	19.28	15.84	"
6	A	13.53	12.45	"
	B	15.27	12.40	"

These results, beyond showing that chroming brings these two hide powders into accord, are probably not of much value, as they are from different samples of extract.

Chroming on the shaker has given very satisfactory results with some hide powders, but others plump so much that they are very difficult to squeeze afterwards. The greatest objection to the method for the use of wet chromed hide, as outlined in directions sent to collaborators, is the length of time required to chrome the hide—that is, three days. The referee considers this a serious objection, as it will delay analyses unless hide can be kept satisfactorily when chromed. This method, at best, is an experiment.

Since sending the samples experiments have been made in order to determine whether the time can not be shortened without disadvantage.

Mr. Brown's experiments along this line follow.

These results show that there is no necessity for chroming hide longer than one day, at least, for the three powders tried, and if any one has worse samples for the official method than B and Freiberg they are unfortunate. One or two chemists have expressed the opinion that three days' chroming is necessary, or at least better, but have not submitted any results that support their views.

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TABLE 12.—DETERMINATION OF NON-TANNINS WITH REGARD TO TIME INVOLVED (BROWN and ALSOP).

Hide powder	Chestnut extract (0.8 gram solids per 100 cc.) Per cent.	Chestnut extract (0.4 gram tannins per 100 cc. Per cent.	Quebracho extract (0.8 gram solids per 100 cc. Per cent.	Quebracho extract (0.4 gram tannins per 100 cc.) Per cent.
Brown				
Vienna, unchromed.....	14.28	14.47	8.72	9.23
Freiberg, unchromed.....	16.54	16.78	—	10.71
No. B, unchromed	16.47	17.12	—	—
Vienna, chromed 3 days..	14.06	13.83	8.27	8.42
Freiberg, chromed 3 days.	14.76	14.34	8.20	8.23
No. B, chromed 3 days ...	14.04	13.91	—	8.41
Vienna, chromed 1 day...	14.01	14.02	—	8.44
Freiberg, chromed 1 day .	14.71	14.62	8.14	8.46
No. B, chromed 1 day....	14.02	13.92	—	8.27
Dry chromed	14.11	14.18	—	8.71
Average for chromed hide.....	—	—	—	8.42
Average for chromed hide Mr. Wilson's table, No. 5.....	—	—	—	8 44
Alsop				
Vienna unchromed	—	14.46	—	—
B, unchromed	—	16.69	—	—
Vienna, chromed 3 days..	—	14.01	—	—
B, chromed 3 days.....	—	13.81	—	—
Vienna, chromed 1 day...	—	14.05	—	—
B, chromed 1 day.....	—	13.80	—	—

In Table 8 the results by one day and three days' chroming show about 0.3 per cent. lower non-tannins for the longer period. Mr. Hurty gets lower results by long chroming with larger quantities of chrome. Assuming that Mr. Craighill's dry-chromed powder chromed one day is free from solubles, as well as the hide chromed three days by Mr. Hurty, who states that he tested for soluble hide in filtrate with negative results, what warrant is there for chroming any longer, even if the non-tannins may be lowered? The great advantage of the hide powder method is that it approximates the conditions in the tannery.

Vienna hide has been considered the standard by most chemists, because until recently it gave concordant results and a non-tannin filtrate free from tannin and almost free from soluble hide. No other hide powders that the referee knows of fulfill these conditions as well. Some differ widely from Vienna and almost always give higher non-tannins. Chroming causes these powders to give concordant results with a somewhat lower non-tannin in the case of Vienna hide when 3 grams chrome

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per 100 grams hide are used. The referee believes that the best way to chrome is the method that will bring concordance with the least variation from the standard now in use.

Mr. Craighill says that his experiments point to 3 grams per 100 grams of hide as the best amount to use. This bears out experiments of the referee. The referee does not believe that there will be any material difference in hides chromed one day or three days with that amount of chrome alum, but if chemists use varying amounts of chrome, much of the benefit of the method will be lost.

The referee urges that the chroming of hide powder one day (twenty-four hours), with 3 grams of chrome alum per 100 grams of hide be made the official method. This method will not delay analyses to any extent. Hide started one afternoon will be ready the next day. It is generally most convenient to dissolve extracts in the afternoon and analyze the next day.

He also advocates a provisional method for dry chromed hide and recommends that it be carefully experimented with next year; also that an effort be made to interest hide powder manufacturers to find out if it is possible to produce this material in marketable quantities of a satisfactory quality.

The referee has decided to advocate the adoption of 0.35 to 0.45 gram tannin per 100 cc. as the official method for solution of tanning materials. A comparison of Tables 1 to 4 seems to warrant this decision, which is scientifically correct, in theory at least. It is the method adopted by the European association and brings our methods that much nearer in accord. The majority of collaborators who expressed any opinion declared in favor of it. Prof. H. R. Procter states:

We have found in practice that the difficulty of choosing a quantity of material, of which the tannin will fall within these limits, to be largely an imaginary one.

In regard to the volume of solution to be evaporated for the various determinations the following comments have been made:

Mr. Krug: I am not favorably impressed with the use of 50 cc. for evaporation. This volume of solution leaves very little limit for error, and only doubles the errors already present and so far unavoidable.

Mr. Wilson: The method for non-tannins involves a residue too small when 50 cc. is used for evaporation. In the writer's opinion, the method should state a range of weight for the residue for different materials. This can be accomplished by substituting 100 cc. for 50 cc. in some cases. It appears to the writer that for total and soluble solids the residue as now given need not be changed.

Mr. Teas: I do not approve of the weaker dilution, nor the use of 50 cc. for evaporation, the errors being increased when so small quantities are to be weighed.

Mr. Yocum: I am not in favor of the use of the smaller volume, the unavoidable errors being increased by its use and the shorter time re-

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quired for evaporation in no wise compensating for the greater errors introduced.

MR. REED: The error resulting from the evaporation of 50 cc. is multiplied, whether this error occurs in pipetting or in weighing. Without doubt this is the only disadvantage. The error is proportionately larger in the case of the non-tannins. To offset this we have the following advantages:

(1) The time gained in the performance of the analysis.

(2) Time saved in process of filtration.

(3) The error from oxidation upon reduction of time in drying is lessened.

In my opinion, the advantages of using 50 cc. more than offset the disadvantages.

MR. SMALL: I am in favor of using 50 cc., it being my opinion that more accurate work can be done with these smaller quantities.

MR. CRAIGHILL: I am unqualifiedly in favor of 50 cc. for evaporation, believing it to be more accurate. The longer time required for drying the larger residues has objections, to say nothing of the point of decomposition.

Mr. Brown and the referee, when making analyses of the official samples, did each in duplicate; also evaporated two 50 cc. portions for each determination from the same solution. The result of their work, which involved a large number of weighings, shows that no closer duplicate weights can be obtained than when 100 cc. is used. The referee agrees with Mr. Yocum that the time gained in evaporation of the smaller volume does not at all compensate for the greater errors introduced. He does not remember seeing any figures to show that errors introduced by oxidation are lessened by the smaller volume.

Mr. Reed states as an advantage the time gained in process of filtration. He gives in his report the following experiment and its results:

Twenty-nine solutions of quebracho extract were tested, each as follows: Five grams kaolin added to portion of each solution, stirred, and 150 cc. passed through and discarded. The 50 cc. following (the fourth) and the two following portions (the fifth and sixth) were evaporated. The comparison was made in order to prove whether we were obtaining, as nearly as possible, the correct soluble solids by the evaporation of the fourth 50 cc. according to the then official method.

SOLUBLE SOLIDS IN QUEBRACHO EXTRACTS FROM THE EVAPORATION OF THE FOURTH, FIFTH, AND SIXTH 50 CC. FILTERED PORTIONS OF THE SAME SOLUTIONS AFTER DISCARDING THE FIRST 150 CC. PASSING THROUGH.

Number of quebracho solutions used	Number soluble solids tested	Kaolin used in grams	50 cc. portion evaporated	Number instances giving highest per cent. soluble solids	Percentage of instances giving heaviest soluble solids
29	29	5	Fourth.....	13	44.83
	29	5	Fifth	11	37.93
	29	5	Sixth	5	17.24

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This record does not show as great uniformity as could be desired. The percentage is in favor of the fourth 50 cc., but not very markedly so. The result would have been of greater value if the time of contact had been taken in each instance.

These figures the referee considers an argument in favor of the evaporation of 100 cc., which lessens the error in the determination of soluble solids.

The method proposed by Mr. Wilson, involving the use of 100 cc. for some non-tannin solutions and 50 cc. for the other determinations, does not seem advisable nor one likely to be followed if adopted.

Mr. Carr, in his report last year, said:

Owing to the sensitiveness of tanning materials to the heat employed in drying, it is believed that the use of volumes yielding residues of from 400 to 500 mg. is preferable to volumes giving greater residues. It is believed that if, instead of 100 cc., 50 cc. shall be used for total and soluble solids, the resultant weight may be dried to constant weight in less time and at less risk of decomposition or oxidation.

The method as modified by him also involves the use of weights for non-tannins as low as 40 mg.

It is interesting in this connection to note that the time for drying was not shortened.

The quantity of material advocated by the referee for solution of tanning materials involves residues somewhat heavier than the above when 100 cc. is used, but in his opinion 50 cc. would cause residues too small for the best results, and therefore the use of 100 cc. for all evaporations is advocated.

Mr. Krug reports the following experiments on various methods of drying:

TABLE 13.—DETERMINATIONS OF SOLIDS WITH VARIOUS METHODS OF DRYING.

Official Quebracho Extract.

Method of drying	Total solids			Soluble solids		
	A. Per cent.	B. Per cent.	Mean Per cent.	A. Per cent.	B. Per cent.	Mean Per cent.
10 hours in vacuo, 70° C.	85.05	84.95	85.00	76.32	76.11	76.22
8 hours in air bath, 100° C.	84.47	84.74	84.61	74.95	75.05	74.90
8 hours in air bath, 110° C.	83.26	84.21	83.74	74.74	74.74	74.74
24 hours in water bath 98° C.	85.37	85.37	85.37	74.74	74.74	74.74
Official Chestnut Extract.						
10 hours in vacuo, 70° C.	46.17	46.51	46.34	44.69	44.97	44.83
8 hours in air bath, 100° C.	47.94	48.06	48.00	47.14	47.09	47.12
8 hours in air bath, 110° C.	44.80	46.17	45.49	43.77	45.14	44.46
24 hours in water bath, 98° C.	46.06	46.80	46.43	44.12	44.17	44.15

On these results Mr. Krug makes the following comment:

The comparative moisture determinations show considerable variation, and I believe this to be due to some loss by oxidation when the determinations were made by drying in air. Drying at 110° is in almost every case

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unsatisfactory, giving wide variations, and this temperature is no doubt too high and causes decomposition.

Last year one method for drying was changed from eight hours at 100° to 103°, in air bath, to eight hours at 100° to 110°. No reasons are assigned for the change in temperature, and the referee knows of none that justify it.

The temperature obtainable in a hot-water oven does not exceed 100°. Therefore it seems that no method of drying should exceed 100° unless it is made the only one to be used. The referee believes that the time stated for drying in the method is in excess of that required for practical purposes, especially if the weaker solution be adopted as official.

The results on total solids in the reports received from collaborators vary so much when dried under the same conditions that any comparison of the results based on different methods of drying are not of much value.

In the report on tannin presented by J. H. Yocum in 1898 Mr. Eachus contributed some valuable results on this subject.*

The greatest variation in per cent. of tannin, in Mr. Eachus's table, 0.43 per cent., is between duplicates both dried eighteen hours. The experience of the referee is that prolonged drying causes greater variations in weights between duplicates, due, probably, to decomposition or oxidation. It also gives slightly lower weights in most cases, but does not cause any material diifference in the percentage of tannin.

The following changes in the method are recommended: From eight hours at 100° to 110°, in air bath, to six hours at 100°, and from twenty-four hours to eight hours at the temperature of boiling water, which means practically a hot-water oven where the temperature is rarely above 98°. The referee has had no experience with drying extracts in vacuo, therefore can express no intelligent opinion as to the time required.

With the exception of two, the collaborators expressed no opinion on the question of filtration for soluble solids. Mr. Craighill expresses himself as opposed to the use of kaolin or any other assistant. In a report on the subject, from Mr. Reed, the following table is found:

TABLE 14.—INFLUENCE OF TIME OF FILTRATION AND PROPORTION OF KAOLIN UPON SOLUBLE SOLIDS (REED).

Solid quebracho extract	Concentration Grams in 100 cc.	Kaolin Grams	Total solids Per cent.	Soluble solids Per cent.	Reds Per cent.	Volume of filtrate cc.	Time of contact Minutes
Analysis 1.....	9½	10	84.75	74.95	9.80	200	290
Analysis 2.....	9½	5	84.75	75.43	9.32	200	215
Analysis 3.....	9½	2½	84.75	75.73	9.02	200	150
Analysis 4.....	6	10	85.01	77.37	7.64	200	175
Analysis 5.....	6	5	85.40	77.93	7.47	200	135
Analysis 6.....	6	2½	85.40	78.37	7.03	200	120
Analysis 7.....	6	1¼	85.40	78.70	6.70	200	110
Analysis 8.....	6	0	85.01	[1]78.80	6.20	200	90

[1] Shows trace cloudiness.

* See Bul. No. 56, Div. of Chem., Dept. of Agric., p. 100. This JOURNAL 15, 32, (1920).

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Mr. Reed comments on these results as follows:

By comparing the time consumed in filtration for soluble solids in the case of the more diluted solution with that of the less diluted, it will be observed that the former gives a much more rapid filtration than the latter when the amounts of kaolin are the same. At the same time the more dilute solution requires a less amount of kaolin to produce the requisite clear solution. Thus we have by employing a more diluted solution been able to reduce the amount of kaolin and the time of contact of the solution with the filter paper.

As the official method now stands for soluble solids "10 grams kaolin, previously washed in a portion of the solution, may be used when a clear filtrate can not otherwise be obtained." That this does not fully cover all possible contingencies must be true from the very fact that of two extracts of the same tanning wood one may give a clear filtrate without the use of kaolin while the other may require it. If we are comparing two such extracts for their relative tannin content, and in one case use no kaolin and in the other 10 grams of kaolin, as the official method indicates, we obtain results which are certainly not justly comparable; *i. e.*, if we employ 10 grams of kaolin to obtain a clear filtrate, where a certain amount of kaolin is absolutely necessary, we should use 10 grams of kaolin for the solution where no kaolin is required. This must be true if with the same solution we obtain such widely divergent results in soluble solids with different proportions of kaolin. As stated by the referee in last year's report, "Absorption is largely a function of the time the solution is in contact with the paper," and this being true the addition of an equal amount of kaolin to a solution not of necessity requiring it will surely tend to make the time of contact more nearly the same as that of the solution requiring it. To recapitulate, it is the reporter's opinion that there should be some method suggested so that a uniformity in time of filtration for soluble solids could be brought about, taking into consideration the varying results with different proportions of kaolin as shown.

It may be stated that by the methods now in use clear filtrates can not be obtained with some extracts with any degree of certainty or within a reasonable time without the use of some assistant. In the absence of some better method, this association should either make no determination for reds, which is manifestly unjust, or it should adopt some method involving the least error that will insure a clear filtrate in all cases, and that method be followed for all extracts. The method as adopted last year advocated the use of barytes. Almost without exception chemists who have tried this method have discarded it. The following method is proposed:

To 2 grams of kaolin add 75 cc. of the tanning solution, stir, let stand fifteen minutes, decant as much of the liquid as possible, add 75 cc. more of the solution, pour on filter, keep filter full, reject the first 150 cc. through, evaporate the next 100 cc. Double-pleated S. & S. No. 590, 15 cm. filter paper shall be used.

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Two grams of kaolin is sufficient to clarify extracts, therefore there is no need of using 10 grams, as the larger amount retards the filtration, and in addition introduces other errors. Although by no means perfect, this method has given good results, and does not materially affect results on an extract that can be filtered clear without kaolin.

The referee has made no experiments with the optional method for soluble solids, and therefore expresses no opinion about it.

The following modifications of the official method (Bulletin 46, revised, page 79, VIII, methods) for the analysis of tanning materials are recommended:

II. QUANTITY OF MATERIAL.—First line, read "give from 0.35 to 0.45 gram of tannins per 100 cc. of solution." Sixth line, read "give from 0.35 to 0.45 gram of tannins per 100 cc. of solution."

III. MOISTURE.—(b) 1. Read: "For eight hours at the temperature of boiling water in a steam bath."

(b) 2. Read: "For six hours at 100° in an air bath."

IV. TOTAL SOLIDS.—For 50 cc. read 100 cc.

V. SOLUBLE SOLIDS.—Read: "Double-pleated filter paper (S. & S. No. 590, 15 cm.) shall be used." Proceed as follows: To 2 grams of kaolin add 75 cc. of the tanning solution, stir, let stand fifteen minutes, decant as much of the liquid as possible, add 75 cc. more of the solution, pour on filter, keep filter full, reject the first 150 cc. through, evaporate the next 100 cc.

VI. NON-TANNINS.—Read: "Prepare 20 grams of hide powder by digesting twenty-four hours with 500 cc. of water, adding 0.6 gram of chrome alum in solution. This solution to be added, one-half at the beginning and the other half at least six hours before the end of the period. Wash by squeezing through linen; continue washing until the wash water does not show any precipitate with barium chloride. Remove as much water, etc."

The remaining operations are identical with the official method, except that "100 cc." is read for "50 cc."

To VI add the following optional method:

To 14 grams of dry chromed hide powder in a shaker glass add 200 cc. of the tanning solution; let stand two hours, stirring frequently; shake on shaker fifteen minutes; throw on funnel with cotton plug in stem; let drain; tamp down the hide in funnel; return filtrate; filter until clear; evaporate 100 cc.

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REPORT ON MEETING OF THE INTERNATIONAL ASSOCIATION OF LEATHER TRADES CHEMISTS, 1901.

By W. H. Krug.

Bulletin No. 67, U. S. Dept. Agric.

The International Association of Leather Trades Chemists met at Liège, Belgium, on August 28, 1901. The changes made in the method used by that association were as follows:

(1) The adoption of Freiberg hide powder, the maximum cellulose content to be 20 per cent., and the manufacturer to mark each delivery with the percentage it contains.

(2) The adoption of the A. O. A. C. method for used tanyard liquors.

Professor Procter formally proposed the adoption of the Association of Official Agricultural Chemists' method as official, but the motion was lost, the comparative results obtained by the members indicating that it was not more exact than the filter-tube method. The subject of filtration was discussed at length, and the association was forced to the conclusion that in the determination of the soluble solids a perfectly clear filtrate is absolutely necessary. The members expressed much dissatisfaction with paper No. 605, owing to the fact that it does not give uniform results and the filtration is exceedingly slow, but no change was made pending experiments which are to be reported at the next meeting. In connection with the adoption of Freiberg hide powder a sub-committee was named which will formulate methods for testing the suitability of various hide powders and for determining the moisture, ash, cellulose, and nitrogen in them. Dr. Paessler presented a series of results obtained with chromed hide powder and showed that it possesses no special advantages. This was confirmed by Professor Procter and others. The difficulties encountered in the analysis of extracts which have been decolorized by the addition of bisulphites was discussed and it was shown that the addition of a trace of hydrochloric acid to the solution gave results from 2 to 4 per cent. higher than by the ordinary method. No definite conclusion was reached by the association, Professor Procter stating that the present rules permitted the addition of acid, provided this was stated in the report.

Professor Procter presented a lengthy report dealing with the differences which to-day exist between the International and Association of Official Agricultural Chemists' methods. With a considerable number of comparative experiments as a basis he arrived at the following conclusions:

(1) That rapid cooling of the diluted extract on the whole gives a somewhat higher result for soluble solids than slow cooling, and, furthermore, a smaller mean error, so that the advantage appears to lie with the International method, which also has the merit of rapidity and convenience.

(2) That flat-bottomed dishes possess no advantage over round-bottomed dishes, the residues drying as rapidly in the latter as in the former.

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(3) That the variations, which American chemists claim to be caused by the method of cooling, are more probably due to the greater oxidation which attends the longer period of drying prescribed by the Association of Official Agricultural Chemists' method.

(4) That errors may often be caused by inaccuracy of the weights used.

(5) That the determination of the soluble solids must be made on an absolutely clear filtrate to obtain concordant results, the kaolin filtration being probably the best method known for this purpose.

(6) That the compulsory adoption of an expensive quantitative paper like S. & S. No. 590 is not warranted, it being probable that any paper free from soluble matter will be fully satisfactory when kaolin is used.

(7) That the filter-tube method gives the lowest result in non-tannins, the Association of Official Agricultural Chemists' method averaging from 2 to 3 per cent. higher and the accuracy being somewhat greater with the former, although in both cases the mean error may be neglected.

(8) That the Association of Official Agricultural Chemists' method is less affected by differences in the hide powder, especially when the powder is faintly acid.

As previously stated, the association decided not to abandon the filter-tube method, though the Association of Official Agricultural Chemists' method was adopted for spent liquors.

The question of using a chromed hide powder has occupied the attention of American chemists for some time, and it may be of interest to quote from Professor Procter's report.

Experiments have been made on the use of chromed hide powder, as proposed recently by Weiss, though they are not so exhaustive as might be desired. Powder was chromed in several ways, using a basic solution of chrome alum, added slowly over three days, and also by drumming for half an hour * * * but none of these gave as good results as that chromed according to Weiss's original directions.

Weiss's statement was confirmed that the powder became less absorbent when strongly pressed, a lot of powder accidentally pressed to 30 per cent. of water giving with chestnut extract and Weiss's method of digestion overnight a result of 10.1 of non-tannins, as compared to 7.1 by the same method when the water was reduced to only 90 per cent. With the same extract the filter method showed only 6.3 per cent. It was found that shaking by the machine for 20 minutes gave somewhat lower results in non-tannins than standing overnight. In each case powder equal to 7 grams of dry powder per 100 cc. was employed.

It was found that while the powder with 30 per cent. of moisture was quite sweet and good after three months, that with 90 per cent. was putrid in a week. I am far from saying that this use of chromed hide powder is not worth further experiment, but it does not seem to have reached a completeness which would justify us in considering it as an official method, and where the shaking machine is used it is more troublesome and probably

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not more exact than untreated hide powder. It is also most probable that that the presence of chrome and formaldehyde would alter the ratio of absorption between different tanning materials at least to some extent.

In conclusion, I desire to read a letter recently received from Professor Procter and would suggest that the method of determining the absorption—correction for the filter paper in the determination of the soluble solids described therein—be made the subject of an investigation by the referee for the ensuing year. The letter is as follows:

LEATHER INDUSTRIES LABORATORIES, THE YORKSHIRE COLLEGE,
Leeds, October 25, 1901.

DEAR MR. WILEY: We are experimenting here with a method for correcting the results of filtration of tanning liquors through different papers, which in view of the early meeting of the Association of Official Agricultural Chemists I hasten to communicate to you, although we have not yet tested it at all fully. The principle of the correction is that we adopt such a method of filtration in the first instance as will give a perfectly clear filtrate with the material in question. Suppose, for instance, that to do so we employ paper 590 and 3 grams of kaolin. In order to establish the correction for the particular material and for this special mode of filtration we make a second filtration, using double paper 590 and 6 grams of kaolin. Naturally this work must be done at least in duplicate to avoid experimental errors. In the second filtration we have practically double the true absorption which takes place in the first, and consequently the second liquor will leave a smaller residue than the first one. The difference between the two, then, is the correction required, and must be added to the result with the single filtration in order to compensate for the loss with 1 paper and 3 grams of kaolin. Of course, there is the theoretical objection that the liquor on passing through the second paper is already weaker and presumably gives up somewhat less tannin to the paper, but a little numerical consideration will show that this correction of a correction is quite too small to influence the results of analysis. The method is easy of execution, the filtration through double papers taking but little longer than that through a single one, and from the work we have already done it is evident that the results if not absolutely accurate at least very much diminish the error which the paper introduces. Of course, if this should turn out on practical experience to be the case it at once unifies our methods with regard to filtration, since for any particular extract we shall use the paper we find most satisfactory and make the corresponding correction, of which in many cases one determination will serve for a whole series of analyses, the whole thing being only a question of tenths per cent.

At the meeting of the International Association in Liège the absolute necessity of filtering to perfect clearness was strongly insisted upon, and I very fully indorse this as being an essential to concordant results. Of course, it may happen that in some cases a tanning material contains small quantities of coloring matter or some special substance which is

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fully absorbed by the first paper, and in this case that substance must necessarily be reckoned as insoluble matter. Whether these cases ever arise is uncertain, but some conclusion may be arrived at by experimenting with extract infusions and liquors which are optically clear without filtration. In this case the whole loss should take place in the first filtration and no loss or a much smaller one in the second. I have not, however, yet come upon any cases which support this idea.

Hoping that some of your chemists will take up the matter and confirm or condemn the method which I suggest,

I am yours, faithfully,

HENRY R. PROCTER.

REPORT ON TANNIN.

By W. H. Teas, Referee.

Bulletin No. 73 U. S. Dept. Agric.

For this year's experimental work the following samples were sent to 18 chemists: Chestnut extract, quebracho extract, and a union liquor.

The work on the extracts consisted in a comparison of results on soluble solids obtained by the use of single and double filter paper (S. & S. 590). Analyses were made according to the official method, the optional use of any good grade of filter paper for non-tannin filtration being the only change.

DOUBLE AND SINGLE FILTERS.

The question of the comparative influence of different amounts of filter paper in contact with tannin solutions upon the results on soluble solids led to these experiments. It is understood that the filter paper does absorb tanning matter, and this being the case, it is argued that the least amount of paper essential to a clear filtrate should come in contact with the solution. Mr. H. C. Reed undertook some experiments along these lines which are more complete than circumstances will permit reporting in detail. His results as regards filter paper known as 590 S. & S. were as follows:

Results on soluble solids with single filter for fourteen tanning solutions, ranging from a clear solution of a tanning extract to quebracho solutions, showed an average increase of 0.47 per cent. over the results secured on the same solutions by the use of double filters; the official method was used in all cases.

The results of the work on this year's samples show an increase in soluble solids where the single filter was used over the average of double filter results on soluble solids, of 0.23 per cent. in the case of the chestnut extract, and an increase of 0.74 per cent. on the quebracho extract. This, too, despite the fact that the analyses were made by different chemists and the evaporation and drying took place under different conditions. In general the individual results bear out the indications of the average,

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there being but two results (both on chestnut extract) in which the soluble solids with double paper exceeded results from single paper. The single filter method requires a longer time for filtration and there is a possible chance of error here, unless all possible precautions against evaporation are taken.

On the question of double or single filter paper, some of the collaborators have expressed themselves as follows:

Mr. Wilson says: "I am convinced that 590 S. & S. single with assistance will trap all insolubles, and it is certainly desirable to have the least possible amount of paper in contact with a tannin solution. The difference is not so great in quick filtering solutions like chestnut, but on slow filtering solutions, rich in insolubles, the difference is marked, which should, we think, bring the 590 single strongly into favor."

Mr. Reed favors the single paper.

Mr. Alsop is of the opinion that single paper will remove all insolubles.

Mr. Alden says: "I hope the double filter will be retained, for there seems to be a considerable difference in the case of quebracho. The filtrate was not clear, as in the case of the double filter."

Turbid filtrates have caused the referee to hesitate to recommend the adoption of the single paper; with the double paper, kaolin, and ordinary care, a clear quebracho filtrate can always be secured. Single paper has not always given clear filtrates and sometimes necessitates two or three trials. If the single filter gives as clear a filtrate as the double, then there can be no question as to the correctness of the higher soluble solids results obtained from the single filter. It is only with unclarified quebracho and similar extracts that the annoyance of turbid filtrates occurs; and as it is questionable whether the analysis of such extracts represent their true value in the tannery—because of the dissolving temperature, and strength at which they are used differing greatly from the conditions in the laboratory—it is extremely important that every particle of insoluble matter be determined.

Apropos of this matter, I desire to quote from Mr. Alsop's report to the referee: "I regret to say that I did not notice that you said to take 10 grams quebracho to the liter. I took 25.32 grams for 2 liters, which, while it falls within the limits prescribed by the method, will probably make my results low in tannin." This statement indicates a condition of affairs which is patent to every chemist who has had any experience with the analysis and use of extracts rich in insolubles.

With the advantages and disadvantages of the single filter paper in mind, I advocate its trial for determinations of soluble solids, provided that all dryings shall be made from perfectly clear filtrates.

Acid Determinations.

Acid determinations by three methods were made on the union liquor sent out. I may here remark that formaldehyde was used on the liquor to keep the initial amount of acid constant. The distillation method directions were as follows:

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Take 125 cc. of original liquor, distill over 100 cc., and titrate distillate with phenolphthalein and N/10 sodium hydrate. Call this result 80 per cent. of total volatile acid in the liquor (*i. e.*, 80 per cent. of acid in 100 cc. of original liquor).

This method was formerly in use in the laboratories of the United States Leather Company, the procedure of calling the acid in the first 100 cc., 80 per cent. of the acid in 100 cc. of the liquor having been determined on, after a series of experiments made some years ago. The standard method for comparison used in these experiments I am unable to give, as the data are not now at hand. It has been regarded as a fair comparative method for the volatile acid determination in tan liquors, the low results having been attributed to the percentage of lactic acid in the liquor, which results from this method would not show.

At the suggestion of the referee, Mr. H. C. Reed made some experiments on the determination of acid in acetic and lactic acid solutions of known strength by the three methods indicated by the referee. In these experiments commercial grades of acid were used; 125 cc. of acetic and lactic acid solutions and 125 cc. of a solution of the two combined, in the ratio of 50 per cent. each, were distilled to 100 cc. distillate, and the distillates titrated with N/10 sodium hydrate. The following results were obtained:

Acetic acid solution containing 0.664 per cent. showed 0.69 per cent.

Lactic acid solution containing 0.58 per cent. (as acetic) showed 0.019 per cent.

Acetic and lactic (equal parts) containing 0.623 per cent. (as acetic) showed 0.371 per cent.

Experiments conducted on the same lines, but with chemically pure acids, gave the referee the following results:

Acetic solution containing 0.84 per cent. showed 0.44 per cent.

Lactic solution containing 0.88 per cent. showed 0.011 per cent.

Acetic and lactic solution containing 0.86 per cent. showed 0.22 per cent.

Acid determinations made by any distillation method can not include the lactic acid content, as it can not be distilled unchanged, but is broken up by heat into lactic anhydride, and ultimately into lactide. Distillation methods involving the distilling over of nearly all the original liquor subject the acid to the danger of decomposition by the greater heat of the parts of the still not covered by the residue.

Of the distillation methods used in this year's experiments, Mr. Wilson writes: "The chief objection to the distillation method is in assuming the 100 cc. of distillate to contain only 80 per cent. of the total acid in the liquor, although the result so obtained seem to bear out the assumption."

Determinations by the Kohnstein-Simand method were made by heating 100 cc. of the original tan liquor with 3 to 4 grams of freshly ignited chemically pure magnesia, filtering, removing lime, and determining gravimetrically the magnesia in the filtrate. Theoretically this is probably the

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best method, but it is too tedious and requires too much care and time to be of practical use in a laboratory where many acid determinations are made. The filtration of the liquor is slow, and, in the case of many heavy liquors from acid hemlock tanneries, it is impossible unless the funnel is kept hot by means of a hot-water jacket.

Mr. Reed reports: "Determinations were made (Kohnstein-Simand method) in triplicate upon solutions of acetic and lactic acids and a combination of the two, in the ratio of 50 per cent. each, with the following results:

"Acetic acid solution 0.663 per cent. by titration showed 0.664 per cent.

"Lactic acid solution 0.536 per cent. by titration showed 0.581 per cent.

"Acetic and lactic acid solution 0.579 per cent. by titration showed 0.623 per cent.

"The method does not permit of very rapid determinations, and even if it gives more accurate results, which is doubtful, the writer believes it should be discarded for this reason."

Mr. Wilson says: "The magnesia method might be, when properly handled, the most accurate of the methods under consideration. It has the objection, however, of being tedious, and is open to sources of error in manipulation."

For the charcoal methods 100 cc. of the original liquor were diluted to 500 cc. and the diluted solution was used for the methods (*a*) and (*b*):

(*a*) To 100 cc. of the diluted liquor add 2½ grains of animal charcoal, stir thoroughly every fifteen minutes for two hours, throw on filter and titrate an aliquot portion of the clear filtrate with N/10 sodium hydrate, after the additon of about 200 cc. of distilled water.

(*b*) To 100 cc. of diluted liquor add 2½ grains charcoal, bring to boiling point with constant stirring, filter, and titrate.

For comparable results by the charcoal methods it is essential that the animal charcoal shall be free from acids and carbonates; the charcoal sent out with the samples is an imported product and has given even results for some six months past.

Results by these methods are generally lower than the actual acid content, but the difference with every lot of charcoal of the best grade is constant, and if a correction for this difference be made the result is nearly absolute.

The objection to method (*a*) seems to be to the length of time the charcoal is in contact with the liquor; results from method (*a*) are invariably lower than those obtained from method (*b*). The difference, however, is not due entirely to the time of contact, but to some extent to the decreased volume of liquor caused by evaporation while heating. Mr. Reed reports on his experiments with acid solutions with these methods as follows:

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Two samples of charcoal were used in these experiments, one furnished by the referee and the other an impure grade purified by treatment with hydrochloric acid and washing. Methods (*a*) and (*b*) were used, the latter modified by using a flask with tube condenser and frequent shaking. Charcoal from referee is marked (*c*) and that prepared by writer (*d*):

TABLE 1.—COMPARATIVE RESULTS OBTAINED WITH TWO CHARCOALS.

Volume of solution	Acetic acid solution (c)	Acetic acid solution (d)	Lactic acid solution (c)	Lactic acid solution (d)	Combination (50 per cent. acetic, 50 per cent. lactic) (c)	Combination (50 per cent. acetic, 50 per cent. lactic) (d)
40 cc. solution required without treatment N/10 NaOH	cc. 8.85	cc. 8.85	cc. 7.75	cc. 7.75	cc. 8.30	cc. 8.30
40 cc. solution required by method (*a*) N/10 NaOH	6.95	7.70	5.3	7.55	5.90	7.65
40 cc. solution required by method (*b*) N/10 NaOH	7.1	7.95	5.35	7.65	5.95	7.80

It will be noted that charcoal purified by the writer gave almost theoretical results in the case of the lactic acid solution, but with the acetic acid solution considerable loss of acid resulted. By treatment of the acetic acid solution with various amounts of a charcoal and calculation of the loss of acid from a given weight of charcoal, practically theoretical results were obtained.

The referee's experiments along the same lines with the same charcoal as that sent out resulted as follows:

TABLE 2.—COMPARISON OF TWO CHARCOAL METHODS.

Volume of solution	Acetic acid cc.	Lactic acid cc.	Acetic and lactic cc.
40 cc. solution required without treatment, N/10 NaOH	10.8	10.2	11.4
40 cc. solution required by method (*a*) N/10 NaOH	9.4	8.8	9.9
	9.4	8.8	9.8
	9.35	8.8	9.9
	9.4	—	—
40 cc. solution required by method (*b*) N/10 NaOH	9.9	9.15	10.1
	9.9	—	—

The use of purified bone black was suggested in the instructions in making determinations by this method, the process consisting of treatment with dilute hydrochloric acid, subsequent washing and drying, and a final heating almost to the point of combustion. Mr. Reed's results with charcoal treated in this manner are given above. The referee heated some charcoal similar to that accompanying the samples and on the liquor sample made the following determinations: By method (*a*), 0.40 and 0.40 per cent.; by method (*b*), 0.42 and 0.415 per cent.

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From the table given on the determination of acid by the three methods, the Kohnstein-Simand method seems to give the least concordant results. As stated above, the slow filtration and the number of distinct operations necessary seem to afford too many opportunities for error.

The distillation method as used in this work depends too much on the 80 per cent. hypothesis. In this case the results are close to those from the charcoal methods, but it has been the referee's experience that many liquors showing a certain percentage of acid by the distillation method will give almost double when treated with charcoal.

It seems to be the opinion of the majority of the collaborators that the charcoal methods are sufficiently accurate and comparable for adoption. The following comments were made on this point:

MR. WILSON: It seems to the writer that the simple charcoal method is sufficiently accurate for the control of yard liquors.

MR. REED: The writer is inclined to the charcoal methods for the determination of total acids, preferring method (*b*) with the variation of a flask and tube condenser.

Mr. Small, differing from these views, writes: "The methods outlined (Kohnstein-Simand excepted) introduce such large errors in the amount of acid contained, by reason of the treatment necessary to get clear liquors, that they are valueless save for comparison." He advocates the acid method in which the tannin is precipitated by gelatin and the resulting liquid titrated, using spot test with litmus for end reaction.

TABLE 3.—RESULTS OF EXPERIMENTS WITH CHESTNUT EXTRACT, USING SINGLE S. & S. 590 FILTER PAPER.

Analyst	Moisture Per cent.	Total solids Per cent.	Soluble solids Per cent.	Reds Per cent.	Nontannins Per cent.	Tannins Per cent.
F. P. Veitch	——	43.48	42.93	0.55	17.92	25.01
J. H. Yocum	56.15	43.84	43.52	0.33	19.22	24.30
F. H. Small	56.40	43.36	42.40	0.96	17.43	24.97
C. H. Brown	55.61	43.94	43.23	0.71	17.20	26.03
W. K. Alsop	——	43.72	43.18	0.54	17.46	25.72
Frederick Alden	——	43.35	42.80	0.55	18.42	24.38
H. T. Wilson	56.17	43.48	*42.51	1.02	——	25.78
	56.15	43.53	42.34	1.19	16.73	25.61
H. C. Reed	——	43.76	43.18	0.58	17.57	25.61
C. C. Hildebrand	——	43.33	42.88	0.45	17.23	25.65
W. H. Teas	——	43.43	42.43	1.00	16.92	25.51
	——	43.32	42.36	0.96	16.89	25.47

* Laboratory paper.

	Per cent.
Average soluble solids	42.81
Lowest soluble solids	42.34
Highest soluble solids	43.52
Greatest difference from average	0.71

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TABLE 4.—RESULTS OF EXPERIMENTS WITH CHESTNUT EXTRACT, USING DOUBLE S. & S. 590 FILTER PAPER.

Analyst	Moisture Per cent.	Total solids Per cent.	Soluble solids Per cent.	Reds Per cent.	Nontannins Per cent.	Tannins Per cent.
F. P. Veitch	——	43.48	42.62	0.86	17.92	24.70
W. H. Krug	——	43.04	41.52	1.52	15.80	[1]25.72
J. H. Yocum	56.15	43.85	43.74	0.12	19.22	24.51
F. H. Small	56.40	43.32	42.29	1.03	17.49	24.80
C. H. Brown	55.61	43.94	43.00	0.94	17.20	25.80
W. K. Alsop	——	43.72	43.07	0.65	17.46	25.61
Frederick Alden	——	43.51	43.03	0.48	18.60	24.43
H. T. Wilson	56.17	43.48	[2]42.26	1.22	16.73	25.53
	56.15	43.53	42.33	1.15	16.73	25.60
H. C. Reed	——	43.76	42.91	0.85	17.57	25.34
C. C. Hildebrand	——	43.33	42.25	1.08	17.23	25.02
W. H. Teas	——	43.43	42.32	1.11	16.92	25.40
		43.32	42.21	1.11	16.89	25.32

[1] Dried five hours in vacuo, at 100° C.
[2] Laboratory paper.

	Per cent.
Average soluble solids	42.58
Lowest soluble solids	41.52
Highest soluble solids	43.74
Greatest difference from average	1.16

TABLE 5.—RESULTS OF EXPERIMENTS WITH QUEBRACHO EXTRACT, USING SINGLE S. & S. 590 FILTER PAPER.

Analyst	Moisture Per cent.	Total solids Per cent.	Soluble solids Per cent.	Reds Per cent.	Nontannins Per cent.	Tannins Per cent.
H. T. Wilson	52.49	——	[1]43.02	4.52	——	35.98
	52.44	47.54	43.08	4.46	7.04	36.04
F. P. Veitch	——	48.00	43.68	4.32	7.07	36.61
J. H. Yocum	52.39	47.61	43.28	4.33	9.06	34.22
F. H. Small	52.42	47.10	42.72	4.38	7.25	35.47
C. H. Brown	52.22	47.69	43.28	4.41	7.42	35.86
W. K. Alsop	——	47.41	42.46	4.95	7.56	[2]34.90
Frederick Alden	——	48.03	45.35	2.68	7.39	37.96
H. C. Reed	52.50	47.47	43.39	4.08	7.13	36.26
Harry Gerber	52.13	48.72	46.23	2.49	7.31	[3]38.92
C. C. Hildebrand	——	47.68	43.54	4.14	7.81	35.73
W. H. Teas	——	47.46	44.32	3.14	7.43	36.89
		47.45	44.46	2.99	7.47	36.99

[1] Laboratory paper.
[2] Twelve and one-half grams extract to liter.
[3] Fifty cc. evaporation.

	Per cent.
Average soluble solids	43.75
Lowest soluble solids	42.46
Highest soluble solids	46.23
Greatest difference from average	2.48

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TABLE 6.—Results of Experiments With Quebracho Extract, Using Double S. & S. 590 Filter Paper.

Analyst	Moisture Per cent.	Total solids Per cent.	Soluble solids Per cent.	Reds Per cent.	Nontannins Per cent.	Tannins Per cent.
H. T. Wilson	52.49	——	[1]42.61	4.93	——	35.57
	52.44	47.54	42.23	5.31	7.04	35.19
H. C. Reed	52.50	47.47	42.93	4.54	7.13	35.80
F. P. Veitch	——	48.00	43.40	4.60	7.07	36.33
W. H. Krug	——	48.23	42.20	6.03	6.93	[2]35.27
J. H. Yocum	52.39	47.61	43.00	4.61	9.06	33.94
F. H. Small	52.42	47.09	42.39	4.70	7.30	35.09
C. H. Brown	52.22	47.69	42.83	4.86	7.42	35.41
W. K. Alsop	——	47.41	41.72	5.69	7.56	[3]34.16
Frederick Alden	——	47.75	43.64	4.11	7.17	35.47
Harry Gerber	52.13	48.72	46.05	2.67	7.31	[4]38.74
C. C. Hildebrand	——	47.68	43.16	4.52	7.81	35.35
W. H. Teas	——	47.46	43.02	4.44	7.43	35.59
		47.45	42.97	4.48	7.47	35.50

[1] Laboratory paper.
[2] Dried 5 hours in vacuo at 100° C.
[3] Twelve and one-half grams to liter.
[4] Fifty cc. evaporation.

	Per cent.
Average soluble solids	43.01
Lowest soluble solids	41.72
Highest soluble solids	46.05
Greatest difference from average	3.04

TABLE 7.—Comparison of Results on Soluble Solids.

Results compared	Chestnut		Quebracho	
	Single paper Per cent.	Double paper Per cent.	Single paper Per cent.	Double paper Per cent.
Average soluble solids	42.8	42.58	43.75	43.01
Lowest soluble solids	42.34	41.52	42.46	41.72
Highest soluble solids	43.52	43.74	46.23	46.05
Greatest difference from average	0.71	1.16	2.48	3.04

TABLE 8.—Results With Different Methods of Determining Total Acidity.

Analyst	Distillation Per cent.	Kohnstein-Simand Per cent.	Charcoal (a) Per cent.	Charcoal (b) Per cent.
H. T. Wilson	0.355	0.350	0.397	0.426
			0.393	0.420
H. C. Reed	0.3945	0.4458	0.42	[1]0.4725
F. P. Veitch	0.38	0.60	0.41	0.45
J. H. Yocum	0.40	0.44	0.34	0.35
F. H. Small	0.36	0.65	0.40	0.42
C. H. Brown	0 37	——	0.37	0.43
W. K. Alsop	0.37	0.48	0.36	0.42
Frederick Alden	0.438	——	[2]0.44	——
Harry Gerber	0.37	0.67	0.39	0.44
			0.368	0.4425
C. C. Hildebrand	0.352	——	0.375	0.45
	0.354	——	0.38	0.409
W. H. Teas	0.360	0.53	0.38	0.416
J. H. Norton	0.31	0.73	0.39	0.46

[1] When condenser was used, the result was 0.42 per cent; with purified boneblack it was 0.4125.
[2] Three hours contact.

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RECOMMENDATIONS.

As the official method for total acid in tan liquors for this year, the referee proposes the following:

To 100 cc. of diluted liquor in a flask with tube condenser add 2 grams chemically pure animal charcoal, bring to boil with frequent shaking, filter, cool, and titrate an aliquot portion.

The following provisional method is also proposed:

To 100 cc. of diluted liquor add 2½ grams animal charcoal, stir every fifteen minutes for two hours, filter, take an aliquot part and titrate.

It is convenient to take 40 cc. of the filtrate and titrate with N/10 sodium hydrate, as this amount is soon filtered and admits of rapid calculation.

It is highly imperative that the charcoal be free from acid and carbonates and preferable that it be recently freshened by careful heating. Treatment of impure charcoals with dilute acid, followed by ample washing and then heating, will result in a charcoal which will give good results.

The following modifications of the official method are recommended:

To omit the moisture determination.

To change (*b*) in paragraph III so as to read:

Evaporations shall take place under precisely the same conditions as to contact with steam or with a metallic plate. All dryings called for after evaporation shall be done by one of the following methods, under precisely the same conditions, so that the different residues of each analysis may occupy the same shelves in the drying oven:

1. For eight hours at the temperature of boiling water in steam bath.
2. For six hours at 100° C. in air bath.
3. For five hours in vacuo at 100° C.

V. SOLUBLE SOLIDS, to read as follows:

Single pleated paper (S. & S. 590, 15 cm.) shall be used. To 2 grams kaolin add 75 cc. of the tannin solution, stir, let stand fifteen minutes and decant as much as possible (not on the filter); add 75 cc. of the solution, stir, and pour on the filter; keep filter full, reject the first 150 cc. of filtrate, evaporate and dry next 100 cc. The portion dried for determination shall be perfectly clear and evaporation during filtration must be guarded against.

VI. NON-TANNINS: Two grams kaolin to be used when filtering.

Omit paragraph VIII on testing hide powder, and section (*b*) of paragraph IX.

For next year's work the referee recommends additional experimental work on soluble solids, acid determinations, and on the amount of extract taken for analysis.

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REPORT ON TANNIN.

By G. A. Kerr, Referee.

Bulletin No. 81, U. S. Dept. Agric.

Pursuant to the recommendations made in 1902, the referee sent to 16 chemists samples of fluid chestnut and solid quebracho extracts for the purpose of—

(1) Confirming the use of a single filter-paper in determining soluble solids.

(2) Investigating the Procter correction for filter-paper absorption, as adopted by the I. A. L. T. C.

(3) Ascertaining the effect, if any, of using a specified dilution in comparison with the variation now allowed by the official method.

Samples of acidified hemlock liquor were also sent out, for the purpose of further testing the present provisional method, and also an experimental method, suggested by W. H. Teas, for the determination of acids in tanning liquors.

An effort was made by the referee to procure a dry chromed hide powder for comparison with the present wet hide powder method, but this effort was unsuccessful owing to the impossibility of procuring in time for this year's work, a hide powder which could be dried with the retention of its absorptive qualities.

Study I.

Instructions were given to determine the total solids, soluble solids, and insolubles in samples No. 1 and No. 2, by the association method.* The results returned are contained in Table 1.

TABLE 1.—Determinations of Total and Soluble Solids and Insolubles by the Provisional Method.

No. of determination	Chestnut extract (A)			Quebracho extract (B)		
	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.
1	37.16	36.18	0.98	86.61	79.56	7.05
2	37.43	36.40	1.03	87.61	81.55	6.06
3	37.62	36.92	0.70	88.49	82.00	6.49
4	37.01	36.15	0.86	86.99	81.80	5.19
5	37.78	36.69	1.09	87.50	82.30	5.28
6	37.42	36.35	1.07	86.76	80.48	6.28
7	37.20	36.14	1.06	86.55	79.82	6.72
8	37.73	36.95	0.78	88.72	81.12	7.60
9	37.69	36.43	1.26	88.55	81.57	6.98
10	36.37	35.16	1.21	86.35	80.28	6.07
11	38.37	36.88	1.49	85.09	78.91	6.18
Average	37.43	36.38	1.04	87.20	80.85	6.35
Maximum	38.37	36.95	1.49	88.72	82.30	7.60
Minimum	36.37	35.16	0.70	85.09	78.91	5.19
Greatest difference	2.00	1.79	0.79	3.63	3.39	2.41
Greatest variation from average	1.06	1.22	0.44	2.11	1.94	1.24

* U. S. Dept. Agr., Bureau of Chemistry, Circular No. 8, revised.

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In the soluble solids column, chestnut extract (A), the greatest difference from the average quantity of soluble solids found by 11 analysts is 3.36 per cent. of the whole. In the quebracho extract (B) it is 2.39 per cent. While these figures confirm last year's work with reference to the adoption of the single-filter paper for filtration of soluble solids, they do not convey an adequate idea of the variation between the highest and lowest percentage of soluble solids found by the different analysts.

Under A the greatest variation is 1.79 per cent., and under B, 3.39 per cent. When it is considered that these differences have a direct bearing upon the tannin figure, the weakness of the present method of determining soluble solids is very apparent.

An examination of the columns giving total solids and insolubles reveals a condition equally unsatisfactory, and makes the seat of trouble somewhat uncertain, commencing as it does with a variation of over 5 per cent. and 4 per cent. in the total solids columns, and ending with one of 112 per cent. and 37 per cent. in the insoluble columns, the indication would seem to be that the entire method, as applied to these items, needs revision.

From personal observation and the comments of the collaborators in this work the referee is of the opinion, however, that the method is not entirely accountable for the differences in results, as it has been demonstrated that with close attention to detail of manipulation and operation much more concordant figures than the above can be obtained. Attention is especially called to the necessity for protecting fluid extracts against loss by evaporation while weighing same for dilution; this also applies to the absorption of moisture by pulverized dry extracts.

The drying of residues, and the loss from evaporation that ensues during the filtration of soluble solids, also require closer attention. The error from the latter cause is much greater, apparently, than has been supposed, and the referee would recommend that as a specific means of guarding against it the following be embodied in Paragraph IV, Soluble solids,* of the method: "To guard against loss by evaporation, flasks receiving filtered liquor shall be stoppered with a perforated rubber stopper, and the funnel stem inserted through perforation. Funnels shall be covered during filtration with a glass plate, having an orifice only sufficiently large to admit air required by displacement of liquor."

It is further recommended that the last sentence of Paragraph II, Quantity of material,* be changed to read: "In the case of extract weigh in weighing bottle fitted with ground-glass stopper, such quantity, etc."

Mr. Veitch makes the following comment:

I have never been satisfied that the change from the double filter to a single one, was a wise one, owing to the fact that kaolin is so apt to run through a single paper. It has usually been my experience, even after rejecting the prescribed volume of liquor, that some kaolin still passes through, and may be best seen by carefully tilting the flask in which the filtrate is received.

* U. S. Dept. Agr., Bureau of Chemistry, Circular No. 8, revised.

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STUDY II.

This experiment consists of a trial of the filter paper absorption correction as suggested by Mr. Procter and adopted by the I. A. L. T. C. The following instructions are copied verbatim from the official method of the above association, except that the method of filtration was carried out according to the method of this association.

(*a*) To determine the correction, filter clear about 500 cc. of the tannin solution, of the strength prescribed for analysis. After thoroughly mixing, 50 cc. is to be evaporated, to determine soluble solids (1). A portion of the remainder is then to be filtered in precisely the same manner as for (1), and 50 cc. of the filtrate is to be evaporated for soluble solids (2).

(*b*) Deduct (2) from (1) and the difference found is the correction which must be added to the soluble solids (1) to give the corrected soluble solids.

(*c*) In proceeding with these filtrations use 2 grams (weighed) of kaolin, which is first to be washed with 75 cc. of the liquor by decantation and then washed onto the filter with a further quantity of liquor; reject the first 150 cc. which passes through in each filtration. Keep the filter full and guard against evaporation.

The results in Table 2 indicate the necessity of having ultimately a correction unless a non-absorbent filter paper is secured or the filter paper now in use can be thoroughly tanned by the liquor passing through before the portion necessary for evaporation is taken. At present, however, it is plain, especially in the case of quebracho extract in Table 2, that the method employed to ascertain this correction augments to an exaggerated extent the error already existing in the determinations of soluble solids, which has the same bearing on the tannin content as the correction is intended to have. In consideration of this condition the referee would suggest that until more uniform results are obtained on the items under discussion further experiments in this line be deferred.

In both cases the differences cover a wider range than in Table 1, but with the quebracho extract in Table 2 the differences are abnormal. It seems to be the consensus of opinion that this difference is largely due to loss from evaporation during the extended length of time required to filter the necessary quantity of liquor for the determination. In this connection it is interesting to note that the precautions employed by the various analysts to guard against evaporation do not seem to have been very effective, which fact emphasizes the necessity of adopting specific means for its prevention, as suggested by the referee in discussing the first experiment. The analysts make the following comments:

MR. VEITCH: From the results of studies 1 and 2 it appears that the absorptive power of the filter is not satisfied by filtering 150 cc. of solution. This is particularly apparent in the case of quebracho.

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TABLE 2.—DETERMINATION OF CORRECTION FOR SOLUBLE SOLIDS.

Determination	Chestnut extract					Quebracho extract				
	Total solids Per cent.	Soluble solids (1) Per cent.	Soluble solids (2) Per cent.	Difference Per cent.	Corrected soluble solids Per cent.	Total solids Per ct.	Soluble solids (1) Per cent.	Soluble solids (2) Per cent.	Difference Per ct.	Corrected soluble solids Per cent.
1	37.35	36.35	36.19	0.16	36.51	86.92	79.67	79.23	0.44	80.11
2	37.43	36.45	36.14	0.32	36.77	87.61	81.66	80.49	1.17	82.83
3	37.63	37.33	37.06	0.27	37.60	88.52	84.25	83.48	0.77	85.02
4	36.37	35.32	34.94	0.38	35.70	86.35	80.34	79.89	0.45	80.79
5	36.95	36.15	35.63	0.52	36.67	87.05	81.85	80.49	1.36	83.21
6	37.78	36.69	36.44	0.25	36.94	87.58	82.30	81.95	0.35	82.65
7	37.42	36.63	36.52	0.11	36.74	——	81.30	80.55	0.75	82.05
8	37.37	36.73	36.48	0.25	36.98	86.74	81.01	80.14	0.87	81.88
9	37.45	36.73	36.70	0.03	36.76	88.39	81.72	80.50	1.22	82.94
10	37.64	36.85	36.48	0.37	37.22	88.32	83.40	82.51	0.89	84.29
11	——	37.17	36.82	0.35	37.52	——	80.30	80.15	0.15	80.45
12	——	37.06	36.02	1.04	38.10	——	77.13	76.93	0.20	77.33
Average	37.33	36.62	36.28	0.33	36.95	87.497	81.24	80.52	0.718	81.96
Maximum	37.78	37.33	37.06	1.04	38.10	88.52	84.25	83.48	1.36	85.02
Minimum	36.37	35.32	34.94	0.03	35.70	86.35	77.13	76.93	0.15	77.33
Greatest difference	1.41	2.01	2.12	1.01	2.40	2.17	7.12	6.55	1.21	7.69
Greatest variation from average	0.969	1.30	1.34	0.70	1.259	1.47	4.11	3.59	0.64	4.63

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MR. MOSBAUGH: Just after Mr. Procter published the method I gave it some attention, and obtained satisfactory results in all extracts with the exception of solid quebracho. Nevertheless I am in favor of its being adopted, as it is well known that filter paper absorbs more or less tannin and this method of correction apparently remedies the evil.

MR. REED: Personally I am not in favor of the method.

MR. TEAS: I think the evaporation, taking place during filtration, accounts for the high soluble solids.

STUDY III.

For the third study the following instructions were given; results will be found in Table 3:

Using official samples Nos. 1 and 2 determine total solids, soluble solids, and insolubles in each according to the provisional method, except as to dilution.

(a) For dilution of sample No. 1 use exactly 1.6 grams per 100 cc.

(b) For dilution of sample No. 2 use exactly 0.6 grams per 100 cc.

Weigh out the portion of sample No. 1 for dilution, in a covered vessel, to guard against evaporation. It is preferable to weigh out approximately the quantity required and dilute so that each 100 cc. will contain 1.6 grams of the extract.

It having been suggested to the referee that the range of variation in the quantity of tannin admissible in dilutions according to the association method was too great to give uniform results (there being a difference of over 28 per cent. between maximum and minimum), this experiment was undertaken to determine, by comparison with Table 1, the value of results obtained by using a specific quantity of total solids. Comparing these tables, we find the results to be in favor of the specified quantity test; slightly so in sample 1, Table 3, but more markedly so in sample 2.

The improvement will, perhaps, scarcely justify any change in the official method for the present, but the referee would suggest that the experiment be repeated with varying quantities of extract until it is ascertained whether or not the total solids contained by an extract form a better basis for dilution than the assumed tannin content. As there is evidently some error in drying residues, caused by the varying quantity of total solids in different dilutions, it seems to the writer that it would be easier to adjust the quantity of residue to be dried to meet the present conditions governing drying than to alter the method of drying to suit the difference in quantity of residue obtained by the association method now in use, inasmuch as this item has been more thoroughly worked out than any other in tannin analysis, excepting non-tannins.

STUDY IV.—ACIDITY OF LIQUORS.

For these experiments a sterilized neutral hemlock liquor (specific gravity 1.015), to which 0.15 per cent. of acetic acid had been added, was sent out, and analysis requested by the following methods:

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TABLE 3.—Determinations by Association Method With Modifications as to Dilution.

Determinations	Sample 1 (Chestnut extract, 16 grams per liter) Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Sample 2 (quebracho extract, 6 grams per liter) Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.
1	37.31	36.26	1.05	87.31	81.28	6.03
2	36.95	36.16	0.79	86.75	79.61	7.14
3	36.22	35.23	0.99	88.63	80.76	5.54
4	37.74	37.06	0.68	88.35	81.41	6.94
5	37.73	36.70	1.03	87.60	81.87	5.73
6	36.89	36.09	0.80	86.50	80.51	5.99
7	37.25	36.00	1.25	89.83	80.66	6.17
8	37.30	36.27	1.03	86.80	79.87	6.93
9	37.63	36.49	1.14	87.58	80.56	7.02
10	37.65	36.87	0.78	88.83	82.07	6.76
11	37.65	36.60	1.05	88.88	81.37	7.51
12	37.97	36.68	1.31	——	——	——
Average	37.36	36.36	0.99	87.43	80.90	6.52
Maximum	37.97	37.06	1.31	88.88	82.07	7.51
Minimum	36.22	35.23	0.68	86.30	79.61	5.44
Greatest difference	1.75	1.83	0.63	2.58	2.46	2.07
Greatest variation from average	1.14	1.13	0.31	1.45	1.29	1.08

TABLE 4.—Total Acidity of Liquors as Acetic Acid.

Determinations	Provisional method Per cent.	Experimental method Per cent.
1	0.195	0.161
2	0.178	0.137
3	0.135	0.150
4	0.150	0.156
5	0.183	0.149
6	0.174	0.140
7	0.168	0.144
8	0.156	0.120
9	0.165	0.105
10	0.170	0.120
11	0.180	0.120
12	0.148	0.140
Average	0.1668	0.1368
Maximum	0.195	0.161
Minimum	0.135	0.105
Greatest difference	0.060	0.056
Greatest variations from average	0..318	0.0318

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(*a*) By provisional method, paragraph 8, circular No. 8, revised, Bureau of Chemistry.

(*b*) To 100 cc. of diluted liquor (prepared as in the provisional method) add 2.5 grams chemical pure animal charcoal, stir every fifteen minutes for two hours, filter, and titrate an aliquot portion with N/10 alkali. For results see Table 4.

It will be noted that the provisional method gives results about 11 per cent. higher than theory, and the experimental method the same amount lower.

By referring to Table 4 in the referee's report for 1902* it will be seen that practically the same results were obtained. The percentage of variation from the average is very similar, although the liquor for 1902 evidently contained about twice as much acid as that sent out this year.

In the opinion of quite a number of analysts this provisional method of determining the acidity of liquors is very satisfactory in tannery practice, for which it is almost exclusively used, especially as to the concordance of the results obtained. Notwithstanding this the referee would suggest that further experiments be conducted with reference to the loss of acid presumably held or neutralized by the charcoal in method "b."

Comments of Analysts.

Mr. Mosbaugh: The acid determination I find does not cover the range of liquors found in sole-leather yards. While the results obtained are concordant and uniform, the method is not applicable to liquors higher in specific gravity than 1.030. As it is sometimes necessary to determine the acidity of the new as well as of the sapped liquors, it is impossible to get a filtrate sufficiently clear for titration, unless a weaker dilution is made or more charcoal used, and in either case the results are not as satisfactory as when the same amount of charcoal is used. I find that by carefully using gelatine in connection with charcoal very good results are obtained and approximately the correction as used for charcoal method holds out.

Mr. Stilwell: In titrating liquor in Study IV I used for the alkali sodium hydrate, checking with limewater. I do not get good results when using N/10 soda, and of the three alkalis prefer limewater.

Good results are obtained by using 2 to 2.5 grams of charcoal and running in a shaker for from two to three minutes. Decolorization is satisfactory. The best concentration is 0.2 to 0.25 grams of tannin per 100 cc. of tan liquor.

In addition to the determinations prescribed in Study IV, Mr. Reed also determined the acidity with charcoal furnished by last year's referee (Mr. Teas), with the following results:

(*a*) Provisional method: 2.75 cc. N/10 sodium hydrate to neutralize 40 cc. of solution. Total acidity = 0.206 per cent. as acetic acid.

* U. S. Dept. Agr., Bureau of Chemistry, Bul. No. 73, p. 81.

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(*b*) Cold charcoal method: 2.25 cc. N/10 sodium hydrate to neutralize 40 cc. of solution. Total acidity = 0.169 per cent. as acetic acid.

Method (*a*) using 2.5 grams of charcoal furnished by this year's referee, instead of two grams as provided, gave a clearer filtrate in the former than in the latter case; 2.3 cc. N/10 sodium hydrate to neutralize 40 cc. of solution. Total acidity = 0.173 per cent. as acetic acid.

Method (*a*): 2 grams of charcoal = 0.195 per cent. total acidity.

Method (*a*): 2.5 grams charcoal = 0.173 per cent. total acidity.

Loss due to 0.5 gram of charcoal = 0.22 per cent. total acidity.

Loss due to 2.0 grams of charcoal = 0.88 per cent. total acidity.

Corrected total acidity = 0.195 per cent. + 0.088 per cent. = 0.283 per cent.

Recommendations.

The only recommendations are those given under Study I, page 88. Suggestions as to future work are also made under the several studies.

Mr. Stilwell: I would like to suggest that 9 hours' extraction be made official. In ordinary tannery practice it does not seem advisable to extend the time very much over 8 hours, though I think that 10 hours is about the normal practice at present. There is a tendency in some portions of the trade, however, to extend the time of leaching considerably. By continuing the extraction for 24 hours or longer very different results are obtained. As 10 hours is about the general practice, I think approximately that figure could be inserted in the method without any difficulty.

Mr. Veitch: I am heartily in favor of what has been said; in tannery practice 10 hours is sufficient. But the point I want to make, Mr. President, is that it is not wise for us to adopt any change without first trying it.

Mr. Stilwell: I agree to that. Ten hours is the normal practice at present. At the same time I am rather anxious to secure some action prohibiting anything over 24 hours' leaching.

Mr. Veitch: This discussion will put the matter on a good basis until some action can be taken. The unnecessary prolonging of the extraction should be stopped.

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REPORT ON TANNIN

By G. A. Kerr, Referee

Bulletin No. 90, U. S. Dept. Agric.

In accordance with the conclusions drawn from last year's work and the suggestions made by the referee, the following lines of work were taken up this year and investigations pursued with more than ordinary interest.

(I) The analyses of chestnut, quebracho, and hemlock extracts by the present provisional method. This work was sent out for the purpose of securing a basis of comparison for the special work.

(II) A special study with a view of ascertaining the causes of variation in soluble solids and insoluble matter found in extracts.

(III) The analyses of fresh and leached bark and fresh chestnut wood, according to the laboratory method of each individual collaborator. The referee, being aware of the lack of uniformity in the results returned by different analysts and consequent dissatisfaction among manufacturers employing the services of chemists, considered it advisable to ascertain the status of this particular branch of tannin determination in order that such faults as might be found to exist could be corrected and a method which would yield more uniform results and greater accuracy developed.

(IV) The further investigation of the provisional methods for determination of acid (acetic and lactic) in yard liquors.

(V) A further test to confirm the recommendations made last year regarding the necessity of protecting solutions during manipulation against changes caused by evaporation.

STUDY *I.* COMPARATIVE WORK WITH THE SO-CALLED OFFICIAL METHOD.*

Comparing the relative difference in results contained in Tables 1-3, analyses of chestnut, hemlock, and quebracho extracts, it seems that in the case of chestnut extract alone the present association method comes within the limit of acceptance.

The results returned on the hemlock and quebracho extracts, though an improvement over previous years, still leave much to be desired in the line of accuracy, especially regarding the items of solubles and insolubles. The non-tannin figure, which previous to the adoption of chromed hide powder was the greatest source of error, is now the most uniform, and, excepting instances where faulty manipulation is obvious, or variations clearly traceable to other sources interfere, the results on this item, herewith submitted, confirm previous work relative to the value of chromed hide powder.

*[NOTE BY THE EDITOR.—This method, being the one exclusively used by the association for tannin determinations, has come to be known as "official," but it has never been formally adopted by the association as such, as was explained in the report of the proceedings of the nineteenth convention (Bureau of Chemistry, Bul. 73, pp. 174-175). The editor has therefore corrected this report to read "provisional" or "association" method in referring to the tannin method given in Bul. 46.]

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TABLE 1.—ANALYSIS OF CHESTNUT-WOOD EXTRACT, BY PROVISIONAL METHOD.

Analyst	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Non-tannins Per cent.	Tannins Per cent.
H. C. Reed	37.40	37.05	0.35	10.90	26.15
W. K. Alsop	37.28	36.94	0.34	10.59	26.35
Yocum Manufacturing Co., C. Eachus	38.14	37.61	0.53	11.38	26.23
Fritz H. Small	37.63	36.84	0.79	10.97	25.87
H. T. Wilson	37.50	36.93	0.57	11.13	25.80
W. H. Teas	37.84	37.09	0.75	11.28	25.81
H. Gerber	38.17	37.97	0.20	[1]12.23	[1]25.74
J. C. Scott	38.50	38.08	0.42	[1]13.12	[1]24.96
A. J. Stillwell	37.73	36.62	1.11	11.61	25.01
C. W. Norris	37.72	37.04	0.68	11.01	26.03
F. M. Loveland	38.20	37.39	0.81	[1]12.69	[1]24.70
E. R. McCarthy	37.41	36.47	0.94	11.10	25.37
Average	37.79	37.17	0.624	11.108	25.85
Maximum	38.50	38.08	1.11	11.61	26.35
Minimum	37.28	36.47	0.20	10.59	25.01
Greatest difference	1.22	1.61	0.91	1.02	1.34
Greatest variation from average	0.71	0.91	0.487	0.518	0.84

[1] Omitted from average, as error is obvious

TABLE 2.—ANALYSIS OF HEMLOCK EXTRACT, BY PROVISIONAL METHOD.

Analyst	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Non-tannins Per cent.	Tannins Per cent.
H. C. Reed	45.40	43.48	1.92	15.01	28.47
W. K. Alsop	45.39	43.25	2.14	14.39	28.86
Yocum Manufacturing Co., C. Eachus	45.90	42.84	3.06	13.92	28.92
Fritz H. Small	45.64	40.86	4.78	14.17	26.69
H. T. Wilson	45.58	42.80	2.78	14.76	28.04
W. H. Teas	45.92	41.08	4.84	15.02	26.06
Harry Gerber	45.29	42.86	2.43	[1]16.90	[1]25.96
J. C. Scott	46.56	44.16	2.40	[1]17.70	[1]26.46
A. J. Stillwell	44.61	41.63	2.98	15.52	26.11
C. W. Norris	45.53	42.00	3.53	15.64	26.36
F. M. Loveland	46.18	43.81	2.37	[1]17.56	[1]26.25
E. R. McCarthy	45.92	43.99	1.93	14.06	29.93
Average	45.66	42.73	2.93	14.72	27.71
Maximum	46.56	44.16	4.84	15.64	29.93
Minimum	44.61	40.86	1.92	13.92	26.06
Greatest difference	1.95	3.30	2.92	1.92	3.87
Greatest variation from average	1.05	1.87	1.91	0.92	2.22

[1] Excluded from average on account of obvious error

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TABLE 3.—ANALYSIS OF QUEBRACHO EXTRACT, BY PROVISIONAL METHOD.

Analyst	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Non-tannins Per cent.	Tannins Per cent.
H. C. Reed	50.31	47.68	2.63	8.54	39.14
W. K. Alsop	50.39	47.65	2.74	8.67	38.98
Yocum Manufacturing Co., C. Eachus	50.63	48.00	2.63	8.67	39.33
H. T. Wilson	50.33	48.11	2.22	8.56	39.55
Fritz H. Small	50.30	47.14	3.16	8.29	38.85
W. H. Teas	50.98	47.59	3.39	8.69	38.90
Harry Gerber	50.23	49.03	[1]1.20	[1]11.92	[1]37.11
E. R. McCarthy	51.03	48.85	2.18	8.95	39.90
J. C. Scott	51.45	48.73	2.72	10.14	38.59
A. J. Stillwell	51.92	[1]51.11	[1]0.81	10.85	40.26
C. W. Norris	51.20	48.80	2 40	8.84	39.96
F. M. Loveland	51.90	48.79	3.11	9.65	39.14
Average	50.89	48.21	2.71	9.08	39.33
Maximum	51.92	49.03	3.39	10.85	40.26
Minimum	50.23	47.14	2.18	8.29	38.59
Greatest difference	1.69	1.89	1.21	2.56	1.67
Greatest variation from average	1.03	1.07	0.68	1.77	0.93

[1] Excluded from average on account of obvious error

STUDY II. SOLUBLE SOLIDS AND INSOLUBLES.

Previous reports having made obvious the necessity for greater uniformity in the results on soluble solids and insolubles which have a direct bearing upon the tannin figure and have shown little tendency toward permanent improvement, the referee appointed a special committee for research along this line, the members of which were Messrs. F. H. Small, H. T. Wilson, and H. C. Reed.

Mr. Small first called the referee's attention to a variation he had found to exist in his laboratory in the soluble solid and insoluble figures obtained when analyses were conducted at different temperatures, and submitted results obtained on the official samples of extracts sent out this year. These figures are given below for comparison with results of analyses given under Study I:

TABLE 4.—ANALYSES OF OFFICIAL SAMPLES OF EXTRACT BY MR. SMALL, ILLUSTRATING THE DIFFERENCE IN RESULTS, PRESUMABLY CAUSED BY VARIATION IN LABORATORY TEMPERATURE.

	Chestnut extract		Hemlock extract		Quebracho extract	
Determinations	20° C.	25° C.	20° C.	25° C.	20° C.	25° C.
Total solids	37.63	37.55	45.64	45.58	50.30	50.34
Soluble solids	36.84	37.85	40.86	42.93	47.14	48.48
Insolubles	0.79	0.70	4.78	2.65	3.16	1.86
Non-tannins	10.97	10.85	14.17	14.45	8.29	8.51
Tannins	25.87	26.00	26.69	28.48	38.85	39.97

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TABLE 5.—EFFECT OF VARIATIONS IN TEMPERATURE ON DETERMINATION OF SOLUBLE SOLIDS AND INSOLUBLES IN HEMLOCK EXTRACT

Analyst	Total solids				Soluble solids				Insolubles			
	15° C. Per ct.	20° C. Per ct.	25° C. Per ct.	30° C. Per ct.	15° C. Per ct.	20° C. Per ct.	25° C. Per ct.	30° C. Per ct.	15° C. Per ct.	20° C. Per ct.	25° C. Per ct.	30° C. Per ct.
H. T. Wilson	45.80	45.92	45.62	45.78	41.44	42.28	43.14	43.93	4.36	3.64	2.48	1.85
H C. Reed	45.99	45.99	45.99	45.99	42.19	43.48	43.65	44.22	3.08	2.51	2.34	1.77
F. A. Small	45.89	45 94	45.91	45.94	40.63	41.49	42.44	42.94	5.26	4.45	3.47	3.00
Average	45.89	45.95	45.84	45.90	41.42	42.42	43.08	43.69	4.23	3.53	2.76	2.21

TABLE 6.—EFFECT OF VARIATIONS IN TEMPERATURE ON DETERMINATION OF SOLUBLE SOLIDS AND INSOLUBLES IN QUEBRACHO EXTRACT.

Analyst	Total solids				Soluble solids				Insolubles			
	15° C. Per ct.	20° C. Per ct.	25° C. Per ct.	30° C. Per ct.	15° C. Per ct.	20° C. Per ct.	25° C. Per ct.	30° C. Per ct.	15° C. Per ct.	20° C. Per ct.	25° C. Per ct.	30° C. Per ct.
H. T. Wilson	51.13	51.12	51.14	51.25	47.22	47.15	47.45	48.48	3.91	3.97	3.69	2.77
H. C. Reed	50.50	50.50	50.50	50.50	46.55	47.19	47.27	47.86	3.95	3.31	3.23	2.64
F. A. Small	51.23	50.76	50.66	50.75	46.28	47.42	47.76	48.09	4.95	3.34	2.90	2.66
Average	50.95	50.79	50.76	50 83	46.68	47.25	47.49	48.14	4.27	3.54	3.27	2.69

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Mr. Small remarks in the case of hemlock at 25° C. that the filtered solution was not quite clear. Knowing it had been previously observed that variations were caused by differences in temperature, the referee looked for results of previous research, but was unable to find any figures which indicated the considerable extent of the variation within the limited range of temperature shown by Mr. Small's results. Considering the suggestion thus given of much interest and probable value, the referee decided to submit the question to a committee for confirmation. The results returned by the members confirm Mr. Small's figures in a general way, and prove conclusively that some limitation in temperature must be defined to secure uniformity. In order to test the question, samples of hemlock and quebracho extracts were sent to the committee with the request that the soluble solids and insolubles be determined at 15°, 20°, 25°, and 30° C., respectively. From the tables of results which follow it will be seen that in both cases a constant increase in temperature yields higher solubles and lower insolubles. The average decrease of insolubles at an increase of 15° C. in the case of the hemlock being 2.02 or 48 per cent. of the quantity found at 15°, and in the case of quebracho 1.5 or 37 per cent. of the quantity found at 15° C., while a practically corresponding increase in the solubles is found. It need scarcely be suggested that under like circumstances the tannin figure will necessarily follow a similar variation.

The average difference in soluble solids for each 5° of temperature from 15° to 30° C. is shown to be as follows: Between 15° and 20°, 1 per cent.; between 20° and 25°, 0.66 per cent., and between 25° and 30°, 0.61 per cent. The total soluble solids are constantly increasing with rising temperature. The total average difference in soluble solids between 15° and 30° C. is 2.27 per cent., while the average difference in insolubles for 5° of temperature is, between 15° and 20°, 0.7 per cent.; between 20° and 25°, 0.77 per cent., and between 25° and 30°, 0.55 per cent. The insolubles are constantly decreasing with rising temperature. The total average difference in insolubles between 15° and 30° C. is 2.02 per cent.

The average difference in soluble solids for each 5° of temperature from 15° to 30° C., as shown in Table 6, is as follows: Between 15° and 20°, 0.57 per cent.; between 20° and 25°, 0.24 per cent.; between 25° and 30°, 0.65 per cent.—a constant increase. The total average increase in soluble solids between 15° and 30° C. is 1.46 per cent. The average decrease in insolubles for 5° of temperature is, between 15° and 20°, 0.73 per cent.; between 20° and 25°, 0.27 per cent., and between 25° and 30°, 0.58 per cent.—a constant decrease. The total decrease in solubles between 15° and 30° is 1.58 per cent.

The results of the tests made this year must not be considered regarding uniformity, as the work was done during weather conditions which made it extremely difficult to maintain the desired temperatures. They, however, accord sufficiently in a general way to show that the subject is worthy of further investigation, and the referee would earnestly suggest that further experiments be conducted during the coming year, with a view of ascertaining the behavior of tannin solutions under various condi-

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tions. The work, in his opinion, should include experiments to determine the most favorable temperature at which the solution of various tanning materials should be analyzed; means of maintaining such temperature; the effect of cooling and reheating solutions; the effect of varying temperatures of water used for dilution, and the solubility of the reds or phlobaphenes of various tanning materials in relation to temperature.

In order to ascertain, if possible, the probabilities of error arising from this source in laboratories located so far apart as to be working almost continuously under widely differing conditions, the referee sent cards to 16 laboratories requesting a return of the summer and winter temperatures prevailing during working hours. From the figues given below the reader will note that maximum summer temperatures vary 16° C. and the minimum 9° C., while the maximum winter temperatures vary 7° and the minimum 16.5°. With these figures as a basis, it appears reasonable to assume that such differences in temperature to a great extent account for the lack of uniformity existing.

TABLE 7.—VARIATIONS IN LABORATORY TEMPERATURES.

Location	Summer temperature		Winter temperature	
	Maximum °C.	Minimum °C.	Mamimum °C.	Minimum °C.
Huntsville, Ontario	27.2	21.1	23.8	15.5
Milwaukee, Wis.	36.0	18.0	28.0	10.0
Fremont, Mich.	29.0	—	—	15.0
Worcester, Mass.	34.0	15.0	27.0	10.0
Stamford, Conn.	32.0	24.0	25.0	20.5
Lockhaven. Pa.	32.0	21.0	24.0	13.0
Ridgeway, Pa.	43.0	18.0	27.0	4.4
Newark, N. J.	34.4	23.3	23.8	18.3
Chicago, Ill.	27.0	18.0	21.0	15.0
Buena Vista, Va.	38.0	20.0	21.0	21.0
Damascus, Va.	36.0	20.0	26.0	15.0

COLLABORATORS' NOTES ON STUDY II.

MR. SMALL: My results confirm Mr. Wilson's in a general way, though there is no very exact agreement. My laboratory temperature was over 30° C. at one time, which made it very difficult to keep liquors at a constant temperature of 15° C. for the several hours required for the filtrations. I presume had we been better equipped for the work, and had the temperature conditions been more favorable, the results might have run somewhat closer. There certainly seems to be no question but that the temperature feature is an important one, and work on soluble solids should be done within as limited a range as possible.

MR. WILSON: I think that cognizance should be taken of the variations shown by temperature tests, but of course it is impossible to arrive at any definite figures for correction purposes from the limited amount of work done so far, and this work should be carried over for another year, being

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done during the winter months, when it will be much easier to govern the temperature. Probably there will not be much change on chestnut extract, but the large variations in hemlock indicate the need of closer control of temperature. I suppose any extract rich in reds will show wide variations. * * * All filtrations were made in funnels surrounded by water jackets 2 inches thick, in which water of desired temperature was constantly kept by replenishing from a larger reservoir of like temperature. Temperatures did not vary more than 1° in the water jacket, except in case of quebracho at 15°. Filtrations at low temperatures were extremely slow. Receptacles for filtrates were kept corked according to the recommendation in previous instructions.

MR. REED: Looking at the results from any standpoint, it is evident that the temperature in filtration has considerable to do with the resulting soluble solids, but before recommending that the solutions be filtered at certain temperatures, I would suggest that we consider the effect of cooling the solutions to a fixed temperature, permitting them to return to room temperature, filtering and noting whether under these circumstances the resulting soluble solids will not be practically uniform. I think that if the solution is cooled to about 20° C. and the temperature allowed to rise to that of the laboratory (provided of course that the temperature must rise in order to come to that of the room) the insolubles would not again return to solution. You will observe that my results on the quebracho show but slight differences on soluble solids between 20° and 25°, and I note that Mr. Wilson's results show the same thing.

STUDY III. ANALYSES OF BARKS AND WOOD.

Twelve analysts participated in this section of the work, and the tabulation of their results show just that many variations in the course of procedure at one or more of the important stages of the analyses.

Reviewing the tables and beginning with the analyses it is apparent that in the case of the three first items (total solids, soluble solids, and insolubles) the chief source of difference is attributable to one or more of the following causes: The preparation of the material to be analyzed before extraction, the conditions under which extraction is conducted, the degree of extraction practiced, the quantity of material used, the volume of water employed, or the method and extent of dilution after extraction is completed.

The next item, non-tannins, as in the case of extracts, shows greater uniformity, though the difference, relative to the total percentage of soluble solids, is out of all proportion. Referring to Table 1, it will be seen that the greatest difference in the average non-tannins found in the official sample of hemlock extract is only about 6 per cent. of the whole, whereas in the leached hemlock bark it is 30 per cent. The error is greater in the case of the ultimate figure, tannin, this being accounted for by the differences in the second and third items.

Leaving the results and taking up the data relative to methods, the referee calls attention to the remarkable variations in the quantity of

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material used for extraction, and the soluble extractive contents of the final dilution, ranging in the case of spent bark from 0.106 gram to 0.6764 gram per 100 cc. of solution. The difference is not quite so great in the case of fresh hemlock bark and fresh chestnut wood, but it is not quite clear that it is altogether customary to be goverened in detail by the provisional method, especially in the analysis of spent materials. There is in several instances an apparent lack of attention to the requirements. This point, however, is not without its value, as it tends to demonstrate the stability of the powder as now prepared.

The majority of the analysts used the automatic syphon Soxhlet extractor, two, a percolation method, one, the regular Soxhlet, one, the Procter method, and one, not specified. The time of extraction ranged from 8 to 16 hours.

Summing up the results, it is evident that a more detailed method covering preparation of material, quantity of material to be used, extraction, and quantity of soluble extractions relative to volume is desirable. Accordingly, your referee has drawn up the following provisional method. This is not by any means submitted as a perfected method, but rather as a basis for future investigation.

PROPOSED PROVISIONAL METHOD FOR BARKS, WOODS, LEAVES, ETC.

I. *Moisture Determination.*

Immediately upon receipt of sample, grind or crush as finely as possible 25 grams and dry for 12 hours at 100° C., reweigh, and calculate difference as water.

II. *Preparation of Sample for Extraction.*

Barks, woods, leaves, and other tanning materials, such as nutgalls, myrobalans, etc., should be dried sufficiently to facilitate grinding and then ground to such a degree of fineness that the sample will pass through a sieve of 14 meshes to the inch (linear).

In case of a coarser residue being left after sieving, it should be reground until the entire quantity passes through the sieve. A style of grinder should be used that will make a granular preparation of the desired size, not finer. An excess of dust and very fine particles must be guarded against in order that a rapid and complete extraction may be obtained.

III. *Quantity of Sample to be Used for Extraction.*

Such a quantity of the material to be analyzed should be taken as will yield a sufficient volume of liquor having a specific gravity of 1.0025 at 15° C. Should the gravity of the liquor prove greater than the above, dilute to the desired point with water at about 80° C. If, however, it should prove impracticable to obtain from spent material the necessary volume of liquor of the gravity specified, the gravity should be taken and the quantity of hide powder used to precipitate the tannin reduced in proportion.

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IV. *Extraction of Sample.*

The extraction may be carried out in any form of extractor that will give complete extraction, with a yield of not more than 1 liter of liquor. A temperature of 100° C. should be maintained throughout the entire operation, except in the case of sumac and starch-bearing materials when a maximum of 80° C. will be found better, and extraction continued until the resulting liquor shows no precipitation with gelatin solution, according to the provisional method for testing non-tannins. Should the volume of liquor prove insufficient, dilution should be made immediately with water at 80° C. to as near the mark as possible.

In case of pulverized or finely ground material, such as sumac, powdered nutgalls, etc., the extraction will be materially assisted by thoroughly mixing the sample with glass sand free from iron and matter precipitable or soluble in hot tannin solution.

V. *Total Solids.*

After extraction and final dilution cool slowly to about 20° C., shake thoroughly, allow to stand for one hour, then pipette 100 cc. into a tared dish, evpaorate, dry, and weigh according to the provisional method.

VI. *Soluble Solids, Non-Tannins, and Tannin.*

The determination of these constituents should be conducted by the provisional method.

In all cases it is best to conduct the analyses on a dry basis; that is, with the material dried at 100° C. If the analysis is made to determine the tanning or commercial value, results should be calculated back to the natural condition of the material. In the case of analyses made for comparison between fresh and spent materials, and in controlling tannery or extract manufacturing processes, results are more conveniently calculated and recorded on a dry basis.

Attention must be given to the quantity of hide powder used in determining non-tannins. See Paragraph III, Quantity of sample, etc., above.

Some changes from the usual course of procedure in analyzing crude tanning materials have been made in the method given. In Paragraph I, 25 grams have been specified as requisite for moisture determination, as a smaller quantity can scarcely under any conditions be made representative of the quantity of material involved in the analyses. A sample usually represents the contents of a leach or carload, and not infrequently a considerable portion of a cargo; it will therefore be appreciated that in the case of crude tanning materials it is difficult to procure a truly representative sample, and in the majority of instances it is easy to secure a sufficient quantity of the material to be analyzed to permit the use of at least 25 grams.

Regarding Paragraph II, Preparation of sample for extraction, it is doubtless true that an extraction can not be completed any quicker than the largest particle of the material will yield its extractives. As a rapid

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and complete extraction is desirable in order to obviate an unnecessarily prolonged boiling of the resulting extractives, such as they are subjected to in the case of the Soxhlet extractor, the value of having a uniform preparation and one limited as to the size of the largest particles is apparent, and will probably cover the question of time limit for extraction.

As to Paragraph III, Quantity of sample to be used for extraction, reference to the table covering barks and woods will reveal a great variation on this point, and from any standpoint it is a difficult problem to solve. Considering the question superficially, it would seem there should be no difficulty in compiling a table of quantities embracing the various kinds of crude materials, based upon the quantity of tannin per 100 cc. specified in the provisional method. That this would prove practical is probably true in the case of certain classes of tannin-bearing products, but for our domestic materials, and in the case of spent or leached materials, it seems hardly adaptable.

Your referee instead of specifying a given quantity suggests for the present, and not as altogether a solution of the question, that the liquors resulting from extraction be restricted as nearly as possible to a specific gravity of 1.0025, which will yield with sufficient constancy the quantity of tannin which comes within the limit specified by the provisional method. In this way it may be possible to attain a certain degree of uniformity, as the only precaution necessary is to use a sufficiency of the material analyzed, restricting the volume, of course, within reason. After a little experience, the strength of solution could be kept on the safe side; that is, a little greater than the gravity specified, and regulated by dilution.

A more important advantage to be obtained by governing the strength of these solutions by gravity is that by this means the proper quantity of hide powder can be readily estimated. By referring to the table it will be seen that the quantity used varies from 9.24 to 17.2 grams. In most cases it is apparent that some effort has been made to base the quantity upon the tannin contents of the solution, but with one or two exceptions the quantity relative to the tannin contents as laid down by the present provisional method is inaccurate.

Paragraph IV, Extraction of sample, does not materially change existing methods of procedure, and is designed merely to govern further test work until the efficiency of the various methods of extraction is demonstrated.

Total solids, Paragraph V, while not absolutely essential for a determination of tanning value, has its uses in several industries, and it will further serve in studying the effect of the Soxhlet and other extractors upon the liquors of extraction.

Soluble solids, non-tannins, and tannins, Paragraph VI, assuming that the foregoing items yield to the analyst a liquor in accordance with the provisional method, should be determined in strict accordance with the same.

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TABLE 8.—ANALYSES OF FRESH HEMLOCK BARK (DRIED AT 100° C.).

Analyst	Extractives			Non-tannin	Tannin	Amt. of bark used	Volume of liquor		Strength of solution	Duration of extraction	Method of extraction	Dry hide powder
	Total	Soluble	Insoluble									
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Grams	Obtained cc.	Made up to cc.	Grams per 100 cc.	Hrs.		per 200 cc. Grams
H. C. R.	21.34	18.77	2.57	5.98	12.79	35	800	1,000	0.6569	10	Siphon Soxhlet	12.8
W. K. A.	22.13	19.65	2.48	6.60	13.05	25	800	1,000	0.496	10	"	9.8
Yocum, C. E	20.13	17.45	2.68	6.30	11.15	25	—	1,000	0.4362	9	"	10.0
F. H. S.	22.11	19.03	3.08	6.01	13.02	18	500	500	0.6850	9	"	15.0
H. T. W.	25.11	19.12	5.99	6.61	12.51	35	900	1,000	0.669	12	"	14.87
W. H. T.	21.96	17.98	3.98	6.43	11.55	25	900	1,000	0.494	10	"	10.00
H. G.	—	12.50	—	4.41	8.09	16	625	1,000	0.2002	8	—	13.5
E. R. McC.	21.07	18.79	2.28	4.34	14.45	25	900	900	0.522	8	Percolation	13.5
J. C. S.	—	19.49	—	6.44	13 05	25	1,000	1,000	0.487	—	"	14.27
C. W. N.	21.19	18.99	2.20	6.36	12.63	30	750	—	0.5697	8	Siphon Soxhlet	11.48
F. M. L.	19.81	17.80	2.01	5.95	11.85	20	1,000	1,000	0.256	—	Procter	18.78
Average	21.65	18.14	3.03	5.95	12.19	—	—	—	—	—	—	—
Maximum	25.11	19.65	5.99	6.61	14.45	35	1,000	1,000	0 6850	12	"	18.78
Minimum	19.81	12.50	2.01	4.34	8.09	16	500	9,00	0.2002	8	"	9.80
Greatest difference	5.30	7.15	3.98	2.27	6.36	19	500	100	0.4848	4	"	8.98
Greatest variation from average	3.46	5 64	2.96	1.61	4.10	—	—	—	—	—	"	—

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TABLE 9.—ANALYSES OF SPENT HEMLOCK BARK (DRIED AT 100° C.).

Analyst	Extractives			Non-tannin Per cent.	Tannin Per cent.	Amt. of bark used Grams	Volume of liquor cc.	Strength of solution made up Grams per 100 cc.	Duration of extraction Hrs.	Method of extraction	Dry hide powder per 200 cc Grams
	Total Per cent.	Soluble Per cent	Insoluble Per cent.								
H. C. R.	6.67	6.08	0.59	3.07	3.01	50	1,000	0.304	10	Siphon Soxhlet	12.8
W. K. A.	7.00	6.20	0.80	2.95	3.25	60	1,000	0.372	10	"	9.8
Yocum, C. E.	7.15	6.45	0.70	3.47	2.98	50	1,000	0.322	9	"	10.0
F. H. S.	6.35	5.64	0.71	2.88	2.76	60	500	0.6764	9	"	15.0
H. T. W.	9.01	7.14	1.87	3.99	3.15	62	600	0.559	12	"	10.8
W. H. T.	6.96	6.13	0.83	3.23	2.90	50	900	0.3067	10	"	12.5
H. G.	—	4.03	—	2.71	1.32	70	500	0.1412	8	—	13.5
E. R. McC.	6.03	5.57	0.46	2.51	3.06	50	1,000	—	12	Percolation	11.0
J. C. S.	—	4.76	—	2.56	2.20	60	1,000	0.286	—	—	14.27
A. J. S.	6.08	5.38	0.70	2.75	2.63	50	800	0.3362	10	Regular Soxhlet	17.2
C. W. N.	5.75	5.49	0.26	2.95	2.54	65	750	0.3569	8	Siphon Soxhlet	9.24
F. M. L.	5.63	5.30	0.33	3.76	1.54	20	1,000	0.106	—	Procter	14.73
Average	6.66	5.68	0.725	3.07	2.61	—	—	—	—	—	—
Maximum	9.01	7.14	1.87	3.99	3.25	70	—	0.6764	12	—	17.2
Minimum	5.63	4.03	0.26	2.51	1.32	20	—	0.1060	8	—	9.24
Greatest difference	3.38	3.11	1.61	1.48	1.93	50	—	0.5764	4	—	7.96
Greatest variation from average	2.35	1.65	1.14	0.92	1.29	—	—	—	—	—	—

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TABLE 10.—ANALYSES OF CHESTNUT WOOD (DRIED AT 100° C.).

Analyst	Extractives			Non-tannin Per cent.	Tannin Per cent.	Amt. of wood used Grams	Volume of liquor		Strength of solution Grams per 100 cc.	Duration of extraction Hrs.	Method of extraction	Dry hide powder per 200 cc. Grams
	Total Per cent.	Soluble Per cent.	Insoluble Per cent.				Obtained cc.	Made up to cc.				
H. C. R.	12.01	10.64	1.37	3.59	7.05	45	800	1,000	0.4788	10	Siphon Soxhlet	12.8
W. K. A.	12.15	11.09	1.06	3.78	7.31	30	800	1,000	0.3327	10	"	9.8
Yocum, C. E.	12.09	11.20	0.89	4.20	7.00	—	—	1,000	0.280	9	"	10.0
H. T. W.	14.13	12.45	1.68	5.26	7.19	45	850	—	0.562	16	"	14.87
W. H. T.	11.63	9.71	1.92	3.53	6.18	50	900	1,000	0.4852	10	"	10.00
H. G.	—	8 5	—	2.30	6.20	—	—	—	—	—	—	—
E. R. McC.	9.70	9.01	0.69	2.32	6.69	50	900	900	0.500	8	Percolation	13.5
J. C. S.	—	9.62	—	2.91	6.71	50	1,000	—	0.481	—	"	14 27
A. J. S.	11.16	10.01	1.15	3.41	6.60	25	800	—	0.3125	10	Regular Soxhlet	17.2
C. W. N.	11.35	10.50	0.85	3.52	6.98	65	750	—	0.682	8	Siphon Soxhlet	10.6
F. M. L.	9.23	8.92	0.31	4.02	4.90	20	1,000	—	0.1784	—	Procter	14.61
Average	11.49	10.15	1.10	3.53	6.62	—	—	—	—	—	—	—
Maximum	14.13	12.45	1.92	5.26	7.31	65	1,000	—	—	—	—	—
Minimum	9.23	8.50	0.31	2.30	4.90	20	75	—	—	—	—	—
Greatest difference	4.90	3.95	1.61	2.96	2.41	45	250	—	—	—	—	—

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COLLABORATORS' NOTES ON STUDY III.

H. C. REED: Concerning the analysis of barks, woods, etc., it appears to me advisable that the amounts of the materials to be used for extraction should be specified. * * * If we decide to adopt a method calling for a uniform weight of solids per 100 cc. a table could be readily compiled on this basis. Paessler states that for spent tans 50 grams of the material should be used. I believe that many chemists are using 100 grams and am confident that this is too large a quantity. I am quite positive that it is for the extractor which I use.

Another matter in the spent tan analysis which needs consideration is the amount of hide powder to be used. I have myself been employing half as much wet hide for the spent tan analysis as is specified for the analysis of extracts, fresh barks, etc. * * * I presume that the majority of tannin chemists dry barks, woods, etc., at 100° C. before extraction. It has not been my custom to do this, but to make a separate determination of the amount of water present and to calculate from this the analysis of the dry material.

Again, I believe there should be some uniform method of extraction adopted, specifying possibly the extractor to be used, although it is doubtful if a single apparatus could be used for the extraction of all tanning materials. For example, I do not believe it possible to properly extract quebracho wood by the method that Procter uses, as it requires more drastic treatment. On the other hand, sumac and materials of this character can not be extracted in an apparatus such as is used in the United States Leather Company's laboratory and in my own. * * * I confess I do not entirely like the prolonged boiling of the tannin solution with the Soxhlet apparatus whereby the non-tannins are undoubtedly increased. It would appear probable that after the limit of the extraction was reached the non-tannin would go on increasing at the expense of the tannins. When we stop to consider, there are a great many items entering into the method of laboratory extraction—for instance, the amount of heat, the length of time, and the character of material. I believe an apparatus could be designed somewhat on the principle of the Soxhlet, but with an improvement whereby a portion of the extraction—the earliest off—could be recovered and not submitted to further boiling.

H. T. WILSON: It is customary with us to take enough spent bark to give a liquor as near official strength as possible. Sample No. 2 was too small to give liquor of such strength. Presuming the chestnut wood to be of the same strength as the usual run, we manipulated in the usual manner. The resultant liquor was below the required strength and the quantity of hide powder was higher than called for. Samples were coarser than our regular preparation, especially in the case of the wood. Time of extraction was extremely long, which was no doubt due to the sample being coarse. We extract regularly 10 to 12 hours with good results. It is our opinion that a definite quantity of material should be always taken for extraction, as results are not uniform with varying quantities. The subjoined table on spent bark will illustrate this point.

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TABLE 11.—COMPARISON OF RESULTS OBTAINED USING VARYING QUANTITIES OF MATERIAL.[1]

Number of sample	Quantity of material Grams	Soluble solids Per cent.	Tannin Per cent.	Non-tannin Per cent.
1	20	5.53	2.61	2.92
2	40	5 35	2.58	2.77
3	60	5.07	2.64	2.43
[2]4	—	—	—	—
5	100	4.66	2.49	2.17
6	120	4.78	2.49	2.29
7	140	4.60	2.43	2.17

[1] Made up to 100 cc. for analysis.
[2] Omitted on account of incomplete extraction.

Note the almost constant tannin, while the soluble solids and non-tannins decrease markedly with the increasing strength of liquor. It is our opinion that total solids and insoluble solids determinations on barks and tans are without much value. It is difficult to obtain concordant results, and the process of filtering the hot liquor from the extractor is troublesome and often tedious.

C. EACHUS, *Yocum Manufacturing Company*: Our method for barks is to extract 25 grams dry new bark or 50 grams dry spent bark in the copper Soxhlet extractor for nine hours, cool over night, and make up to 1,000 cc. Make total solids and soluble solids as in extracts. We use 40 grams of squeezed hide powder (chromed) for non-tannins; shake 5 minutes, and finish as for extracts.

W. K. ALSOP, *U. S. Leather Company*: The bark and wood samples were all extracted in a copper extractor at 100° C. The solutions were made up to 1 liter, about 800 cc. being obtained from the extractors. For solids the solutions were shaken and let stand half an hour, then 100 cc. removed. For soluble solids 150 cc. were stirred with 5 grams of kaolin, filtered off, and thrown away; the filter filled again and 100 cc. collected. For non-tannins 200 cc. were shaken 5 minutes with 40 grams of hide powder, 5 grams kaolin added to the glass, then shaken by hand and filtered, 100 cc. of clear filtrate being collected. The amount of dry hide powder used was 9.8 grams. The amounts taken for analysis, 25 grams of fresh bark, 60 grams of spent bark, and 30 grams of wood.

WM. H. TEAS, *Elk Tanning Company*: The barks and woods were extracted in a modified Soxhlet extractor. Fifty grams of wood and spent bark were extracted and 25 grams of new bark. After being weighed into an extractor cup, 1 liter of distilled water was poured on the charge and siphoned through to the reservoir. The extractor was connected up, the flame applied to the reservoir, and extraction continued for 10 hours. The solution was then allowed to cool and liquor amounting to 900 cc. removed, made up to a liter, and the analysis made.

A. J. STILWELL: Private work has convinced me that the method of extraction used by myself is either too severe or the continued boiling of

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the tannin solution is an error. In my opinion no automatic extractor should be allowed that will not approximately conform in results to those obtained by using the old "Procter beaker method." The criterion of the extraction should be the soluble solids contents of the tannin solution and the time of extraction 10 to 12 hours, by agreement.

J. C. SCOTT: The extractions for Study III were obtained by the use of a copper percolator with a perforated copper disk soldered in the bottom of the cylinder. Next to this cotton was pressed so as to hinder the passage of the material extracted, which was used in quantities as stated in the report. A two-holed cork admitted the entrance of steam and at intervals the other hole was used to allow the running in of boiling water, which served to wash out the soluble matter. The extracted liquor was collected in a liter flask until about 600 cc. was extracted. The extraction was continued until the washings showed no color and this liquor, concentrated by boiling until the volume was about 300 cc. (using a funnel in neck of flask to hinder admission of air), was added to that in the liter flask and after 12 hours made up to 1,000 cc.

C. W. NORRIS: (The method used by Mr. Norris is substantially the same as that of Messrs. Alsop and Teas. *Referee.*)

F. P. VEITCH: One of the points which needs immediate attention, in my opinion, is the fineness of material and its effect upon extraction.

(Mr. Veitch's results were not received in time to be included in the comparative table, but owing to their interesting bearing on the subject the referee herewith appends them.)

TABLE 12.—RESULTS OBTAINED BY F. P. VEITCH.

[Total volume of liquor 5 liters, concentrated to 1 liter.]

Material	Total solids Per cent.	Soluble solids Per cent.	Non-tannins Per cent.	Tannins Per cent.	Time of extraction Hours	Dry hide powder Grams	Amount of material Grams
Fresh bark.....	17.43	15.63	4.75	10.88	15	17.10	30
Spent bark.....	3.06	2.93	1.57	1.36	15	14.25	75
Chestnut wood..	8.98	8.58	2.25	6.33	15	14.25	40

G. A. KERR: We use for extraction a percolation system, consisting of a copper cylinder 9 inches long and 2½ inches in diameter, reduced at the top by a cone-shaped shoulder and neck to 1½ inches and at the bottom to one-quarter inch, and fitted with a copper discharge tube of the same diameter. At the lower shoulder a false bottom of finely perforated copper is secured to act as a strainer.

The neck or top is fitted with a rubber stopper, through which is inserted the end of a block tin coil three-eighths of an inch in diameter and consisting in all of some 30 inches of tubing. The upper end of the coil is attached to a main pipe line leading from a water still. In operation this pipe serves to conduct steam from the still, and the tin coil, acting as an air condenser, supplies an ample flow of water at steam heat to the cylinder, where it passes through the material to be extracted and is received in a flask placed directly under the discharge tube of the cylinder.

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In order to avoid washing finely ground particles of the material through the strainer, it is our custom to cover it with a thin layer of cotton. This method was devised by the writer to overcome the difficulty found in using the customary device, and having been found convenient, expeditious, and efficient, its use has been continued. It is understood that this device has also been adopted in other laboratories. There is no trouble in restricting the volume of liquor to 1 liter. A thorough extraction can be easily completed in 8 hours, and prolonged boiling is obviated. The progress of the extraction can at all times be seen and noted and test samples of liquor obtained without disconnecting the apparatus or interfering in any way with the process, and it is applicable to any tanning material. It is our custom to use 25 grams of new bark or wood. The quantity of spent material is governed by the average tannin content of the samples received at the laboratory, and these vary from 1.5 to 3.5 per cent. tannin. In the case of absolutely unknown samples 50 grams dry are used. The quantity of hide powder is governed by the strength of the liquor obtained by extraction.

STUDY IV. DETERMINATION OF ACIDS IN TAN LIQUORS.

The referee herewith presents the report of the special committee on acid determinations, compiled by Mr. Teas, the other members of the committee being Mr. Eachus and Mr. Mosbaugh. The extent of the investigation and the painstaking care with which the work has been executed are strikingly shown by the report. The preponderance of opinion seems to be in favor of officially adopting the present provisional method, with the alternative of employing the cold method should it seem expedient to the analyst to do so.

The referee agrees that a more scientific method might be developed, but if this one yields comparative and concordant results, the necessity of sacrificing something to practicability, especially in laboratories where from 20 to 100 determinations must be made daily, is too apparent to need emphasis. Basing the value of this research upon the ability of the chemists who engaged in it, your referee would recommend that the method receive official recognition.

REPORT OF THE SUB-COMMITTEE ON ACID DETERMINATIONS.

As an outline for the members of the sub-committee on acid determination to work upon, the following suggestions were made:

(1) That determinations of acid in liquors from bark, wood, etc., containing varying quantities of acetic acid, lactic acid, and mixtures of both acids be made, using charcoal with the solution hot and cold, and by shaking cold with the charcoal.

(2) That determinations by these methods be made on aqueous solutions of the same acids.

(3) That various quantities of charcoal and various strengths of tan liquor be used, as far as time permits, in order to make the range of the experiment as wide as possible.

The results of the experiments made on aqueous solutions undoubtedly show that some of the acid is neutralized by the charcoal. This could be

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taken care of by a factor depending on the quality of the charcoal, if the error was proportionately the same with different strengths of acid, and if this condition held true in the case of solutions containing tannin, which, in my opinion, it does not.

TABLE 13.—ACID DETERMINATIONS ON DISTILLED WATER MIXTURES CONTAINING KNOWN QUANTITIES OF ACID (EACHUS).

	15 per cent. solutions		30 per cent. solutions		60 per cent. solutions	
Method	Acetic acid Per cent.	Acetic and lactic acids Per cent.	Acetic acid Per cent.	Acetic and lactic acids Per cent.	Acetic acid Per cent.	Acetic and lactic acids Per cent.
Hot	12	12	25	24	50	50
Cold	11	11	24	23	48	47
Shaker	11	10	24	23	47	47

In the above work 3 grams of charcoal were used, and boiling, stirring, or shaking continued 5 to 10 minutes. It will be noticed that the hot method gives results nearer the actual contents, *i. e.*, higher than the cold methods, and this difference is manifest in all the experiments recorded in this report. Mr. Mosbaugh's figures on the clear acid solutions are slightly higher, which may be accounted for by the fact that he used 2 grams of charcoal. His results follow:

TABLE 14.—ACID DETERMINATIONS ON CLEAR ACID SOLUTIONS OF KNOWN STRENGTH (MOSBAUGH).

[Two grams of charcoal used.]

Acetic Acid Solution.

	Varying strengths of clear acid solutions							
Method	0.8 per cent. Per ct.	0.7 per cent. Per ct.	0.6 per cent. Per ct.	0.5 per cent. Per ct.	0.4 per cent. Per ct.	0.3 per cent. Per ct.	0.2 per cent. Per ct.	0.1 per cent. Per ct.
Hot	0.7305	0.6405	0.5505	0.4485	0.3585	0.2655	0.1695	0.0825
Cold	0.7230	0.6315	0.5370	0.4395	0.3540	0.2565	0.1605	0.0765
Shaker	0.7245	0.6285	0.5445	0.4410	0.3540	0.2565	0.1620	0.0785

Acetic and Lactic Acid Solution.

Hot	0.7305	0.6345	0.5415	0.4455	0.3555	0.2625	0.1695	0.0825
Cold	0.7215	0.6285	0.5340	0.4395	0.3495	0.2550	0.1605	0.0765
Shaker	0.7215	0.6285	0.5355	0.4395	0.3495	0.2560	0.1635	0 0765

The influence of greater amounts of charcoal than the prescribed 2 grams is clearly shown in the following compilation:

TABLE 15.—INFLUENCE OF CHARCOAL ON ACID DETERMINATIONS (MOSBAUGH).

Acetic Acid Solution.

	Varying amounts of charcoal used						
Method	2 gms. Per cent.	2.25 gms. Per cent.	2.50 gms. Per cent.	2.75 gms. Per cent.	3 gms. Per cent.	3.25 gms. Per cent.	3.50 gms. Per cent.
Hot	0.3585	0.3540	0.3468	0.3393	0.3321	0.3276	0.3234
Cold	0.3555	0.3480	0.3408	0.3363	0.3261	0.3186	0.3114
Shaker	0.3555	0.3480	0.3468	0.3363	0.3291	0.3246	0.3174

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Acetic and Lactic Acid Solution

Method	Varying amounts of charcoal used. 2 grams. Per cent.	2.25 grams. Per cent.	2.50 grams. Per cent.	2.75 grams. Per cent.	3 grams Per cent.	3.25 grams. Per cent.	3.50 grams Per cent.
Hot....	0.3495	0.3450	0.3378	0.3303	0.3231	0.3186	0.3144
Cold...	0.3435	0.3372	0.3288	0.3225	0.3201	0.3126	0.3054
Shaker.	0.3435	0.3390	0.3318	0.3246	0.3213	0.3156	0.3084

The results on the determination of acids added to neutral tan liquors newly made are given in Table 16. Mr. Eachus reports having used 12 cc. of liquor diluted to 200 cc. and 3 grams of charcoal, titrating with tenth normal sodium hydrate.

TABLE 16.—ACID DETERMINATIONS ON NEUTRAL TAN LIQUORS OF KNOWN ACIDITY (EACHUS).

Method	15 per cent. solution. Acetic Per cent.	15 per cent. solution. Acetic and lactic Per cent.	30 per cent. solution. Acetic Per cent.	30 per cent. solution. Acetic and lactic Per cent.	60 per cent. solution. Acetic Per cent.	60 per cent. solution. Acetic and lactic Per cent
40° Quebracho Liquor						
Hot	13	14	29	29	58	59
Cold	12	13	27	27	56	59
Shaker	11	11	25	25	54	56
20° Quebracho Liquor						
Hot	14	14	28	28	59	59
Cold	12	13	26	27	58	57
Shaker	11	11	25	25	56	55
40° Hemlock Liquor						
Hot	14	13	29	28	59	59
Cold	13	12	28	27	57	59
Shaker	11	11	27	25	56	57
20° Hemlock Liquor						
Hot	13	13	28	29	59	59
Cold	13	12	28	28	58	57
Shaker	11	11	27	26	57	57
40° Newly Made Oak Liquor						
Hot	14	13	28	28	59	59
Cold	13	12	28	27	58	59
Shaker	12	11	26	25	56	57
20° Newly Made Oak Liquor						
Hot	14	14	28	28	58	59
Cold	13	12	28	27	57	58
Shaker	13	11	26	27	56	57

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TABLE 17.—ACID DETERMINATIONS ON NEUTRAL HEMLOCK LIQUOR CONTAINING 0.92 PER CENT. OF TANNIN (MOSBAUGH).

[Two grams of charcoal.]

Acetic Acid Solution

Method	Varying percentages of acid.							
	0.8 per cent. Per cent.	0.7 per cent. Per cent.	0.6 per cent. Per cent.	0.5 per cent. Per cent.	0.4 per cent. Per cent.	0.3 per cent. Per cent.	0.2 per cent. Per cent.	0.1 per cent. Per cent.
Hot	0.7395	0.6435	0.5445	0.4485	0.3555	0.2595	0.1647	0.0687
Cold	0.7215	0.6285	0.5337	0.4395	0.3465	0.2505	0.1575	0.0645
Shaker	0.7215	0.6285	0.5337	0.4395	0.3471	0.2505	0.1575	0.0651

Acetic and Lactic Acid Solution

Hot	0.7380	0.6360	0.5445	0.4500	0.3570	0.2640	0.1680	0.0780
Cold	0.7260	0.6270	0.5340	0.4380	0.3480	0.2550	0.1620	0.0732
Shaker	0.7260	0.6270	0.5340	0.4380	0.3480	0.2550	0.1605	0.0732

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From the results obtained by Mr. Eachus, and from my own observation of the method, I am convinced that there is little loss of acid when a good charcoal is used in tan liquors containing a moderate quantity of tannin. Where there is a small amount of acid in a weak tan liquor the loss is greater. It is possible that the loss of actual acid is the same in strong liquors as in weak, and if this is so, there must be some compensating influence in the strong liquor which makes up for the loss. If, however, this compensating influence exists, it is not more marked in a 40° liquor than in a 20° liquor, which would seem to indicate that there is really no loss due to good charcoal when a moderate quantity of tannin is present.

Mr. Mosbaugh's results indicate the truth of the contention regarding the comparative effects of the presence of different amounts of tannin. He used a neutral hemlock liquor containing 0.92 per cent. tannin., and his results are but slightly higher than results obtained from same amounts of acid used with distilled water. With 2 grams of charcoal he obtained the results given in Table 17.

On liquor solutions containing 0.4 per cent. of actual acid, and using different amounts of charcoal, the results are shown in Table 18.

TABLE 18.—EFFECT OF USING VARYING AMOUNTS OF CHARCOAL ON ACID DETERMINATIONS ON A 0.4 PER CENT. ACID SOLUTION.

Acetic Acid Solution

	Grams of charcoal used.						
Method	2 Per cent.	2.25 Per cent.	2.15 Per cent.	2.75 Per cent.	3.00 Per cent.	3.25 Per cent	3.50 Per cent
Hot	0.3355	0.3510	0.3468	0.3411	0.3363	0.3309	0.3264
Cold ...	0.3495	0.3420	0.3348	0.3273	0.3231	0.3150	0.3084
Shaker.	0.3495	0.3435	0.3366	0.3303	0.3261	0.3186	0.3114
	Acetic and Lactic Acid Solution						
Hot	0.3555	0.3480	0.3408	0.3333	0.3261	0.3219	0.3114
Cold ...	0.3435	0.3360	0.3288	0.3216	0.3111	0.3156	0.3084
Shaker.	0.3435	0.3390	0.3318	0.3243	0.3201	0.3192	0.3084

While the discrepancy is greater in weak tan liquors and with small amounts of acid, yet the results are comparative. Since in any but weak solutions the results so nearly approach theory, and in view of the simplicity of the method, the facility of operation, and minimum chance of error, as compared with other methods, I favor for the present at least the continuance of the charcoal method. There are other methods probably more scientific, yet from the numerous operations involved the sources of error are multiplied, and in any but expert hands the results are accordingly unsatisfactory.

The results above show that there is nothing, with the possible exception of time, to be gained by the shaking method. Results from shaking are practically the same as from stirring the solutions. The hot-method results more nearly approach theory, but are not more concordant than the cold-method results, and require more time and attention, which is objectionable when a large number of acid determinations must be made.

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In conclusion I wish to again recommend the charcoal methods, hot when possible, and cold when the number of analyses precludes the hot method. The charcoal used must be carefully watched and washed when necessary. The less charcoal used the better will be the results obtained on weak solutions. The dilutions may be the same as for non-tannin work, and the time could be shortened if a weaker solution is used, provided the time for all acid determinations remains the same.

COLLABORATORS' NOTES ON STUDY IV.

C. EACHUS, *Yocum Manufacturing Company*: The work proves conclusively, in my opinion, that the charcoal method is satisfactory. Use 3 grams of charcoal and 12 cc. of liquor made up to 200 cc. with distilled water. Stir or boil from 5 to 10 minutes, filter and titrate 100 cc. of filtrate with N/10 sodium hydrate. Each cubic centimeter of standard sodium hydrate equals 1 per cent. acid. This is the method I followed, and had no trouble getting 40° liquors clear. Shaking has no advantage over stirring. Boiling and stirring give concordant results, and it appears that charcoal does not use up any acid when tannin is present in the acetic or lactic solution.

F. R. MOSBAUGH: In carrying out this work three methods were followed—hot, cold, and shaker. In the hot method the solution was heated to boiling in flask, using return condenser; the cold method, let stand in stoppered flask for 2 hours, shaking every 15 minutes, and in the shaker method gave 3 minutes' shaking in machine. S. & S. filter paper No. 590 and charcoal, rewashed in laboratory before using, were employed. In all cases 2 grams of charcoal (weighed within a milligram) were used. I checked all "chemically pure" acids against my standard solutions and used same flasks for all dilutions, which were made at 21.1° C., and this temperature was maintained throughout. The alkali used was N/10 sodium hydrate. Neutral hemlock liquor made from new bark, containing 0.92 per cent. of tannin, was employed, and in all cases 100 cc. of this was taken for determination, titrating 50 cc. of filtrate.

The object of the first determination was to ascertain the effect of a given amount of charcoal upon liquors containing different amounts of acid, and with this in view eight solutions of acid, strength from 0.1 per cent. to 0.8 per cent. (as acetic) were made up. The second determinations were made to determine the effect of varying amounts of charcoal upon liquors of given acid value. For this, solutions containing 0.4 per cent. of acid as acetic were used, and from 2 to 3.5 grams of charcoal were used, varying 0.25 gram in each determination.

It is found to be necessary to detannize as well as decolorize the liquor, and to accomplish this 1 gram of charcoal is necessary for 100 cc. of liquor containing 0.1 gram of tannin, and when stronger the results are unsatisfactory.

All results are figured as acetic acid, and when a mixture of acetic and lactic acids were used equal parts (as acetic) were taken. Note that cold and shaker methods give results practically the same, but lower than the hot method—also that all methods produce results lower than theory,

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which does not support all of last year's association results in acid determinations. Also the error increases as the acid value of the liquor decreases, and where different amounts of charcoal are used the error is greater in proportion to the amount of charcoal used, all of which goes to show that it would be necessary to regulate the charcoal correction according to the amount of acid contained in liquor, and that the best that can be expected of the method are results to be used for comparison only.

STUDY V. CONFIRMATION OF REFEREE'S RECOMMENDATIONS FOR 1903.

To confirm the recommendations as to the necessity of adopting specific means for the prevention of evaporation during filtration, a request was made for the determination of the solubles and insolubles in the official samples sent out this year—employing the means specified. Nine analysts responded, and upon tabulating their results it is found on comparison with the analyses of the same extract by the provisional method (Table 1) that the soluble solids of chestnut extract are reduced on an average 0.22 per cent., those of the hemlock extract 0.32 per cent., and those of the quebracho 0.01 per cent., while the insolubles are increased to approximately the same extent.

The figures cited do not really give the true difference between results obtained without precaution against evaporation and those obtained under the recommendations, inasmuch as, since the referee suggested this source of error, more care has been taken to avoid variation from this cause.

TABLE 19.—COMPARISON OF PROVISIONAL METHOD, AND REFEREE'S MODIFICATIONS, 1903.

	Chestnut		Hemlock		Quebracho	
Method	Soluble solids Per cent.	Insolubles Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Soluble solids Per ct.	Insolubles Per ct.
Provisional	37.17	0.548	42.73	2.93	48.21	2.71
Referee's modifications, 1903	36.95	0.87	42.41	3.26	48.20	2.57
Difference	0.22	0.322	0.32	0.33	0.01	0.14

TABLE 20.—ANALYSES OF VARIOUS EXTRACTS BY THE PROVISIONAL METHOD, WITH REFEREE'S MODIFICATION, 1903.

HEMLOCK EXTRACT

Analyst	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.
H. C. Reed	45.38	43.47	1.91
F. H. Small	45.64	40.90	4.74
H. T. Wilson	45 52	42.49	3 03
W. H. Teas	45.98	41.28	4.70
Harry Gerber	45.88	43.37	2.51
E. R. McCarthy	45.60	43.84	1.76
J. C. Scott	46.70	43.07	3.63
A. J. Stilwell	44.72	41.40	3.32
C. W. Norris	45.68	41.92	3.76
Average	45.68	42.41	3.26

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CHESTNUT WOOD

Analyst	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.
H. C. Reed	37.39	37.03	0.36
F. H. Small	37.63	36.77	0.86
H. T. Wilson	37.51	36.69	0.82
Harry Gerber	38.22	36.54	1.68
E. R. McCarthy	38.08	37.36	0.72
J. C. Scott	38.51	37.53	0.98
A. J. Stilwell	37.61	36.58	1.03
C. W. Norris	37.64	37.11	0.53
Average	37.84	36.95	0.87

QUEBRACHO EXTRACT

H. C. Reed	50.29	47.65	2.64
F. H. Small	50.34	48.52	1.82
H. T. Wilson	50.41	47.83	2.58
W. H. Teas	51.07	47.10	3.97
Harry Gerber	50.66	48.72	1.94
J. C. Scott	51.45	48.42	3.03
C. W. Norris	51.02	48.34	2.68
E. R. McCarthy	50.99	49.04	1.95
Average	50.87	48.20	2.57

From numerous tests it has been found that a difference of at least 0.5 per cent. soluble solids occurs, which would affect the tannin figure about 0.35 per cent. In any case it is fairly demonstrated that the precautions suggested assist in eliminating error, and your referee advises the adoption of the recommendations.

Observations of Collaborators.

Mr. Wilson: Study V shows the necessity for guarding against evaporation during filtration. The tendency in these tests to reduce the soluble solids emphasizes the necessity of overcoming the filter paper absorption.

Mr. Eachus: By filtering for soluble solids according to your recommendations we obtained 0.5 per cent. lower soluble solids in the hemlock and quebracho samples, but no difference in the chestnut.

Mr. Scott: My results indorse the referee's modification. The use of a ground stoppered weighing bottle is found convenient and necessary to accurate dilutions.

Mr. Stilwell: I find difficulty in transferring rapidly and completely a highly concentrated liquid extract, such as the quebracho received, to a weighing bottle. With this exception I believe the weighing bottle is an improvement.

Recommendations.

It is recommended—

(1) That further research be made, with the object of establishing a limit of temperature at which the determination of soluble solids and insolubles shall be conducted.

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(2) That the method for analysis of barks, woods, etc., as set forth in the foregoing report, be adopted as a provisional method, and trials continued until it has been prefected.

(3) That the present provisional method for the determination of acid in tannin solutions, with the alternative of using the cold charcoal method, receive official recognition.

(4) That the referee for 1905 make a study of present methods of analysis of tannery-yard liquors, especially spent or "sapped" liquors.

(5) That the recommendations submitted in the report for 1903 be embodied in the official (?) method.

The referee desires to thank the members of the tannin section generally, and the members of the research committees especially, for the active interest and assistance rendered during the past two years.

THE EXTRACTION OF TANNING MATERIALS WITH DIFFERENT EXTRACTORS

By F. P. Veitch

Bulletin No. 90, U. S. Dept. Agric.

Owing to the fear that tannin may be oxidized by prolonged boiling, and to the fact that the extraction of certain materials gives maximum results only at low temperatures, a number of forms of apparatus have been used for the laboratory extraction of tanning materials. At present, however, but two extractors are in general use—the Koch or some modification of it, as that of Procter, and a modified Soxhlet devised at the Vienna Research Laboratory and generally known as the Weiss extractor.

There are several objections to each of these extractors. With the Koch extractor the evaporation of the extract, which frequently amounts to from 2 to 4 liters, is a decidedly objectionable feature, requiring considerable time and encouraging to a certain extent the very thing it was designed to prevent, namely, the oxidation of the tannins by boiling. In addition, there is reason to believe that where the tanning material is put in the extractor dry, the most convenient way, there is often some channeling and the extraction is incomplete, as illustrated in the case of the spent hemlock bark given in the table. On the other hand, the Koch apparatus enables one to control the temperature of extraction as no other form does, and its use would seem to be advisable with materials high in starch.

Notwithstanding the fact that Eitner *et. al.*[1] found that the Weiss extractor gave satisfactory results, tanning chemists have generally looked with misgiving on it, fearing oxidation during the long-continued boiling of the extract. Indeed, Hunt,[2] Procter and Parker,[3] and Parker[4] have

[1] *Der Gerber*, 1887, p. 3.
[2] *J. Soc. Chem. Ind.*, 1885, 4: 263.
[3] *Ibid.*, 1895, 14: 635.
[4] *Ibid.*, 1898, 17: 106.

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shown that for many materials less tannin is extracted at boiling than at lower temperatures. The total volume of extract in these experiments was only 1 liter, and it seems possible that longer extraction would have given higher results at the higher temperatures.

The International Association of Leather Trades Chemists has adopted the Koch extractor as official, and Procter (Leather Industries Laboratory Book, and Principles of Leather Manufacture) regards the prolonged boiling of the extracted materials, such as takes place in the Weiss, as inadmissible.

On the other hand, in addition to Eitner *et. al.*, Boegh[5] has found that the Weiss extractor gave higher results than the Koch extractor on oak and pine bark, valonia, sumac, and quebracho wood, and gave lower results on divi-divi and myrobalans. The Weiss extractor is also used in most tannery laboratories in this country in extracting woods and barks, with satisfactory results.

It thus seems that there is considerable difference of opinion as to the accuracy of the results and the losses of tannin obtained with these two methods of extraction. I have therefore endeavored to avoid the difficulties and objections presented by these generally used methods by substituting an extractor with which the evaporation and concentration of large volumes of dilute liquors necessary by the Koch method is avoided, and with which the prolonged boiling of the gradually strengthening extract and its frequent concentration and dilution, as with the Weiss method, is not necessary.

Such an extractor is found in the old and well-known inner tube, continuous extractor, or in the side tube extractor devised by Zulkowsky. With the former the extraction takes place at 100° C., with the latter at 90°-95°. Undue concentration and boiling of the extract is avoided by placing only about 250 cc. of water in the receiving flask, and after the extraction has continued a short time replacing the receiving flask by another containing the same amount of water. This is repeated at longer intervals, until the extraction is completed, the total volume of extract being kept within a liter. If it is desired to extract the first portions at lower temperatures, the heated water may simply be poured on the material in the extractor until 500 cc. have passed through, and the extraction may then be finished at steam heat.

Comparative results which have been obtained with all three forms of extractor are given in the table. The extraction was continued for 2 working days, or about 15 hours, with the Koch extractor being the same for all samples. It was found desirable to thoroughly wet the material before putting it in the continuous extractor thus overcoming any tendency to channeling. A perforated porcelain plate placed on top of the firmly pressed material distributes the condensed water, and, being prevented from rising far by coming in contact with the end of the condensing

[5] *Abstract J. Soc. Chem. Ind.*, 1899, 18: 303.

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tube, prevents loss of material which is apt to be caused by the occlusion and expansion of the air and steam in a finely ground sample.

The results marked (1) were obtained with the Weiss, (2) with the Koch, and (3) with the continuous extractor. The samples include all our generally used native tanning materials except chestnut-oak bark.

In examining the results, total solids may be omitted from consideration, as this determination often includes some of the material which was carried over into the extract. This is particularly true of the results with the Weiss extractor. Although the solid material was given time to settle before drawing out for total solids, not much importance is attached to these results.

Soluble solids were highest by the continuous extraction, except in the case of chestnut wood, where, I believe, the coarseness of the sample was in favor of the Weiss extractor. The Weiss extractor gives higher results than the Koch extractor, except on one sample of tan oak bark. Tannin is highest with the continuous extractor, except with sumac, where, notwithstanding the lowest soluble solids, tannin is the highest when the Koch extractor was used. No conclusion, however, can be drawn from one sample.

As a rule, it appears that where the extraction is continued for some time, all constituents, reds, non-tannin, and tannin, are removed in somewhat larger quantities by using the continuous extractor. Except in the case of sumac, there is nothing to indicate that there is any serious loss of tannin, or rather any material difference in the loss of tannin from any cause, with any of the extractors. While reds and non-tannin are usually higher when the continuous extractor is used, this fact, in the presence of high tannin, is not conclusive evidence that any loss of tannin has occurred. As has been said, apparently larger amounts of all soluble constituents have been dissolved.

The conflicting results obtained by different investigators on the effect of heat on the extraction of tannin and on its oxidation renders further investigation very desirable. Partial explanation of these conflicting results may be found, perhaps, in the small quantity of water used for extraction in the Koch extractor, and also in the custom of beginning the extraction at a low temperature, and finishing at 100°. Procter and Parker in their investigation of the effect of temperature, extraction with only 1 liter of water, and text-books generally, lead one to understand that complete extraction may be secured with 2 liters or less of water. My experience leads me to doubt this very much, as I usually find tannin being removed in considerable quantities, after extracting with 3 or 4 liters for 8 to 12 hours. Further than this, if all the tannin is not extracted at low temperatures, and it is true that high temperatures cause the starches to hold back tannin, it appears reasonable to think that this will occur with the last portions of the tannin as well as the first—and possibly to a greater degree, if the tannins extracted at a higher temperature are more insoluble than those extracted at low temperatures.

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I am inclined to think, from a consideration of the results obtained, that, in the early stages of extraction at boiling temperatures, the tannin is partly precipitated or held back by the gelatinized starch, but that it is entirely dissolved and removed if the extraction be continued long enough. This, I believe, requires about 16 hours. Further investigations with other materials will be made in the leather and paper laboratory of the Bureau of Chemistry.

TABLE 1.—COMPARISON OF RESULTS OBTAINED WITH THREE DIFFERENT EXTRACTORS.

[1, Soxhlet; 2 Koch; 3, continuous.]

Sample No.	Material	Extractor	Total solids Per ct.	Soluble solids Per cent.	Reds Per ct.	Nontannin Per ct.	Tannin Per ct.	Ash Per cent.
2556	Bark of tan bark oak calf	1	27.04	26.06	0.98	——	——	1.66
		2	27.38	26.82	0.56	10.60	16.22	——
		3	29.66	28.68	0.98	——	——	1.44
2532	Bark of tan bark oak calf "Rump bark"	1	45.76	42.72	2.04	——	——	0.60
		2	44.92	42.06	1.86	12.86	29.20	——
		3	47.64	45.48	2.16	——	——	0.25
2592	Pecan shells	1	12.72	12.08	0.64	——	——	——
		2	11.36	——	——	1.73	9.63	——
		3	13.24	12.52	0.72	——	——	——
——	Hemlock bark, new	1	18.47	16.10	2.17	——	——	——
		2	17.43	15.63	1.80	4.75	10.88	——
		3	23.10	19.37	3.73	7.48	11.89	——
——	Hemlock bark, spent	1	——	——	——	——	——	——
		2	3.06	2.93	0.13	1.57	1.36	——
		3	8.29	7.24	1.05	——	——	——
——	Chestnut wood	1	13.68	12.28	1.40	4.75	7.43	——
		2	8.98	8.58	0.40	2.25	6.33	——
		3	12.50	11.20	1.30	3.63	7.57	——
——	Sumacleaves, coarse ground.	1	52.05	49.70	2.35	28.54	21.16	——
		2	47.42	45.72	1.70	20.74	24.98	——
		3	53.57	49.85	3.72	27.29	22.56	——
——	Sumac leaves, fine ground	3	53.12	49.70	3.42	25.92	23.78	——

A DISCUSSION OF METHODS FOR THE ESTIMATION OF TANNIN.

By F. P. Veitch.

Bulletin No. 90, U. S. Dept. Agric.

The method known as the hide-powder method, while not formally adopted as official by this association, is used exclusively for the estimation of tannin in tanning materials. It is well recognized, however, that the method yields inaccurate results. The chief sources of error appear to be a continuous absorption of solids from the solution by the filter

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paper during the preceding determination of soluble solids, and an undoubtedly greater error due to the absorption of coloring matter and other non-tannin matters by the hide powder. The first may produce a minus error, the latter produces a plus error. Experimental demonstration is hardly needed of the fact that hide powder removes other constituents than tannin from tannin solutions brought in contact with it, as such absorption, occlusion, etc., is a common property of all precipitates or other solid matter in contact with solutions of solids, and prolonged washing is frequently required to free them from materials held in this way. Nevertheless we have experiments showing that in addition to tannin most of the non-tannin constituents common to solutions of tanning materials are absorbed to a serious extent by hide powder, as may be seen from the work of Procter and Blocksey,* who found the absorption of gallic acid, quinol, catechol, and catechin when present in solution with gallotannic acid or quebracho tannin was from 44 per cent. to 106 per cent. of the amount present. Dextrin and glucose were absorbed in very much smaller quantities or lowered the absorption of the tannin.

A lively appreciation of these facts, together with the time and work required to obtain results, has greatly stimulated the search for more accurate and quicker methods. The methods and proposals which have appeared as a result of this activity are of such a character that, while I can not offer anything better than the hide-powder method, a few words of criticism and a brief statement of what must be avoided would seem to be timely, and may be of service to many who at first sight are favorably impressed with some of these methods.

Most of the effort has been directed along the lines of the precipitation of tannin by metallic oxides, or along the lines suggested by the Löwenthal method. The effort to determine tannin by precipitation with metallic oxides dates back almost to the infancy of analytical chemistry, and the idea has been tried and abandoned under all kinds of conditions a number of times. There is no doubt that tannin in pure solutions can be determined with metallic oxides, but so far no one has proposed a method which will quantitatively separate tannin from closely related non-tannins and coloring matter such as are always present in solutions of tanning material.

A moment's consideration of the chemical processes involved in dyeing and in the preparation of lake colors is sufficient to convince one that the separation of tannin from the above-mentioned non-tannins is not a simple operation. As a matter of fact, the methods used in mordant dyeing and in the preparation of lakes are the same in principle as those which have been proposed for the separation and estimation of tannin. To make matters worse, tannin is one of the substances which may be used with basic coloring matters to insure a precipitation with metallic oxides, which would not otherwise take place. Such basic colors are not usually present in tanning materials, however. From these facts it is obvious that before we can hope to quantitatively separate tannin from the colored and

* *J. Soc. Chem. Ind.*, 1903, 22: 482.

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colorless non-tannins with which it is usually associated, by the use of metallic oxides, we must develop some means of preventing the co-precipitation or occlusion of these non-tannins or remove them from the tannin precipitate by the use of a wash solution which does not attack the tannin.

Just here it may be said that as the more or less complete removal of coloring matter is common to hide powder, gelatin, and metallic oxides, the tanning value and weight-giving qualities, or in other words, the leather-making qualities, of these coloring matters must be established as a foundation upon which to build any reliable method.

Two methods based on the use of metallic oxides have been proposed during the past two years. Rous* proposes to precipitate tannin with a ferric salt in the presence of a tartrate and acetic acid. The method consists in adding to 50 cc. of tannin solution (containing about 0.4 gram of tannin per 100 cc.), 10 cc. of one-half normal carbonate of soda, 10 cc. of one-half normal ferric sulphate or ferric alum, and 25 cc. of 6 per cent. acetic acid containing 5 grams of neutral sodium tartrate per liter. The whole is stirred vigorously, boiled one minute, filtered, washed free of iron with hot water, ignited, and weighed. The weight of the ferric oxide multiplied by 4.024 equals tannin. The reagents must be so adjusted to each other that when 10 cc. of sodium carbonate and 10 cc. of the ferric salt are mixed, boiled, and filtered, the filtrate must be faintly acid to methyl orange. After boiling five minutes a mixture of the reagents in the proportions used in the determination must remain clear and bright.

The author claimed that the washed precipitate of iron and tannin is of constant composition and assigned to it the following formula—$(C_{14}H_7O_9)Fe$. Washing the precipitate with dilute acetic acid or normal acetic acid dissolved out iron but not tannin. Accurate separation from gallic acid was claimed, but no separation from other closely related compounds was attempted. It was stated that when different quantities of tannin were contained in the same volume of solution the resulting precipitate varied proportionately.

My own work with this method has led to the following conclusions:

With any given tannin solution, maintaining strictly identical conditions as to volume and strength of reagents, duplicates on total weight of precipitate and on the iron it contains are obtained.

Changing the strength of acid in which the precipitation is made changes the amount of iron in the precipitate.

The weight of the precipitate and its iron content do not vary proportionally with the concentration of the tannin solution; that is, when the weight of tannin in the given volume of solution is doubled the weight of the precipitate and of the iron in it is not equally increased.

With different tanning materials the proportion of iron in the precipitate varies greatly, so that it is utterly impossible to establish any relation between the tannin precipitate and the amount of iron it contains.

* *Zts. anal. Chem.*, 41: 717.

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The nature of the relation between the tannin and the iron in the precipitate the writer has not been able to establish. In this we have another close analogy to the lakes, where this relation has never been definitely established.

Precipitation of tannin appears to be complete; at least no precipitate is obtained by adding a few drops of 1 per cent. gelatin solution to the filtrate. A larger quantity of gelatin gives a bulky white precipitate, which is also given by the reagents alone, without tannin. Pyrogallol has been found to precipitate iron in the same way that tannin does, and so has the non-tannin filtrate from sumac. Water-white, non-tannin filtrates from barks, quebracho, and chestnut extracts do not give a precipitate.

Thus in its present form the method is inapplicable to tanning material, but the indication that the iron content of the precipitate may be varied almost at will, without changing materially the organic precipitate, is suggestive, and it may be possible to remove it entirely, leaving tannin or a decomposition product from which tannin may be calculated. I hope to investigate this point further, for even if the method should not be applicable to the estimation of tannins, some light may be thrown on their nature and constitution.

Wislicenus[1] proposes to estimate tannin by absorbing it with an aluminum hydroxide or oxide made by acting on aluminum with 5 per cent. caustic soda and a trace of mercuric chloride. The absorption of the tannin is hastened by mechanical agitation. Gallic acid is also almost completely absorbed, but can be removed by washing. The results obtained when the aluminum tannate was washed agreed fairly well with results obtained by the hide-powder method on a pure tannin, oakwood extract, oak bark, and chestnut extract. The unwashed precipitate weighed too much. This agreement with the hide-powder method is enough to condemn the method so far as accuracy is concerned. If this agreement with the hide-powder method be confirmed on all materials the method may have some claim to consideration, as aluminum hydroxide can be prepared in large quantities and kept indefinitely, thus doing away with one very objectionable feature of the hide-powder method.

Parker and Payne[2] propose to estimate tannin by determining the amount of calcium hydrate neutralized before and after removing the tannin with a specially prepared gelatin solution. This method is a return to the principles of the old Löwenthal method, which has been abandoned chiefly because different tanning materials can not be compared with each other by its use. We do not know that the reducing power of the catechol and pyrogallol tannin is the same, or even that the several tannins of these two groups have the same reducing power for permanganate, or acidity with respect to calcium hydrate. The method consists of adding 300 cc. of N/5 calcium hydroxide to 200 cc. of a clear tannin liquor of the official strength; let stand 7 hours in a stoppered flask, shaking frequently, filter and titrate 100 cc. of the filtrate, using phenolphthalein as indicator, and

[1] *Zts. angew. Chem.*, 1904, 25: 801.

[2] *J. Soc. Chem., Ind.*, 23: 648.

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calculate the quantity of calcium hydrate absorbed by the 200 cc. of tannin solution. This gives the total absorption value of the liquor.

Two hundred cc. of the original tannin solution are then mixed with 100 cc. of N/5 acetic acid and 100 cc. of Collin solution, which is prepared by dissolving 60 grams of good gelatin in 500 cc. of water, warming until dissolved, and treating with 120 cc. of normal caustic soda, heating on the water bath at 90° for 20 minutes, filtering through linen, neutralizing to phenolphthalein 500 cc. of the filtrate with normal acetic acid, and making the whole up to 1 liter, adding 1 cc. of chloroform to preserve it. In the presence of acetic acid the Collin solution completely precipitates the tannin, which is filtered off, 200 cc. of the clear bright filtrate placed in a flask, and 200 cc. of N/5 calcium hydrate added. This is well shaken, allowed to stand for 1 hour, and the absorption of calcium hydroxide determined. After correcting for the acetic acid, we have the absorption minus tannin, which, subtracted from the total absorption, gives the absorption due to tannin, from which the percentage of tannin is calculated. The authors have found that 1 gram of carefully prepared and pure gallotannic acid absorbs exactly 125 cc. of N/5 calcium hydroxide, which corresponds to the following reaction:

$$C_{14}H_{10}O_9 + Ca(OH)_2 = C_{14}H_{10}O_9Ca_4(OH)_8.$$

It is not stated that other tannins have the same value except that 1 gram of ellagic acid is said to absorb 125.9 cc. of N/5 calcium hydroxide. From the total absorption figures results agreeing well with the results by the hide powder method are obtained, while the corrected figures give much lower results.

The authors found that the Collin precipitate of amorphous leather is easily removed from the linen or from the filter paper upon which it is, and if well washed in water, dried, weighed, and the nitrogen determined, the weight-giving capacity of the material is found.

The accuracy of this method will depend largely on two things; first, whether all tannins have the same absorption value for calcium hydroxide as gallotannic acid has, and, second, whether the precipitation of tannin by gelatin or the Collin solution is complete under the conditions of the method. On these points I think one may be pardoned for being somewhat skeptical. There are a number of unexpected statements in this paper. For instance, we note that "pure tannic acid does not precipitate 'Collin' (gelatin) without the addition of a tanning adjunct, *i. e.*, organic acid," and that "the majority of tanning materials depend upon the anhydrous digallic acid content for their activity as tanning agents." "N/5 calcium hydroxide" would be considered a typographical error did it not occur so frequently, and as it is difficult to obtain even an N/20 calcium hydroxide solution, it is important to know just what is meant, for, with different strengths of alkali, tanning materials have a different absorption factor, and no check of the proposed method can be made by others until some explanation of the phrase is given.*

* It has been learned since this paper was written that a N/5 solution of sucrate of lime was meant.

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Perhaps the most interesting statement in the whole paper is that the tannin Collin precipitate can be washed with water, dried at 100°, weighed, and Kjeldahled, thus giving the weight-producing capacity of a tanning material and actually checking the method. If this statement is confirmed it would seem that all difficulties would be solved, but such a thing has never been satisfactorily accomplished before.

For more than a year I have been working at odd moments along lines similar, but not identical, to those of the Parker method, but without definite results—indeed, with rather unfavorable results. An attempt to duplicate the work of Parker and Payne came to nothing on account of inability to obtain a N/5 calcium hydroxide solution. A barium hydroxide solution did not give results near theory on a practically pure gallotannic acid. Admitting the accuracy of the results obtained on pure gallotannic acid by this method, I believe that we must wait for the proof that other tannins have the same reaction with limewater before the method can be regarded as having a practical value.

Although I have made numerous experiments with a good commercial (medicinal) gallotannic acid with chestnut, quebracho, and oak extracts, I have never been able to completely precipitate the tannin with gelatin, using the Parker and Payne method—the filtrate always contains both tannin and gelatin. This, however, may be my fault, and greater familiarity with the method or a correction of the evident error regarding the strength of the limewater, and consequently of the acetic acid, may lead to better results.

In conclusion, while no method is known which promises better results than the present method, we should not rest satisfied with it, but endeavor to devise a substitute which shall have a firmer foundation both in theory and in its relation to tannery practice. With this object in view efforts have been made for some time in the Bureau of Chemistry to obtain a complete precipitation of tannin with gelatin in such form and purity that it may be dried, weighed, and its composition determined. So far they have been unsuccessful, but the investigation has not been abandoned.

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CONTENTS

Elections - - - - - - - - 129
Proposal to Change Section 7 (A) of the By-Laws - - 130
Definition of Total Ash in Leather. By Committee on the Determination of Total, Soluble, and Insoluble Ash in Leather, John M. Seltzer, Chairman - - - - - - - 130
Tabulation of Hydrogen and Hydroxyl Ion Concentrations of Some Acids and Bases. By Arthur W. Thomas - - - 133
The Time Factor in the Adsorption of the Constituents of Chrome Liquor by Hide Substance. By A. W. Thomas, M. E. Baldwin and M. W. Kelly - - - - - - - 147
Synthetic Tannins and their Use in the Tannery. By Professor E. Nihoul 156
Abstracts - - - - - - - - 171

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PROPOSAL TO CHANGE SECTION 7 (A) OF THE BY-LAWS.

The Secretary has received the following proposal to change the by-laws:

Section 7 (A) to be changed so as to read:

> The Association shall consist of active and associate members, the latter having all the privileges of the Association except that of voting on questions of Methods of Analysis or altering the by-laws of the Association.

(Signed) LOUIS E. LEVI,
AUG. C. ORTHMANN.

DEFINITION OF TOTAL ASH IN LEATHER.

By Committee on the Determination of Total, Soluble, and Insoluble Ash in Leather. John M. Seltzer, Chairman.

Upon the request of the Council to the 1919 committee for a definition of the Total Ash in Leather, the question was submitted to the different members of the committee and the following answers were received.

W. K. ALSOP, ELK TANNING CO.

I should say that the ash in leather is the amount of mineral matter left after burning off the organic matter, both in vegetable and mineral tanned leathers.

It is probably desirable to define closely the manner in which the leather shall be burned in order to obtain as uniform results as possible.

J. B. CHURCHILL, AMERICAN LEATHER RESEARCH LABORATORY.

I would say that I do not see how it is possible to define Total Ash whether in chrome or vegetable tanned leather or in any other substance, except in the following way:—The per cent. of Total Ash in any substance is the per cent. of residue which is left upon ignition of that substance to a point where no free carbon remains. It is self-evident that this percentage will vary

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in some cases with intensity and length of ignition and this variation will depend to a great extent upon the nature of the inorganic constituents of the material to be ignited. I do not think that any more precise definition can be given unless we should wish to define the exact conditions under which ignition should take place.

In special cases where the exact nature of the inorganic constituents of the substance to be ignited is known, it may be possible to judge the amount of such materials as they originally existed in the substance to be ignited by the amount of Total Ash found; but I do not believe that we can go further than to say that the Total Ash is simply the per cent. of residue left after ignition under some specific condition and that no further meaning can possibly be given to the value thus derived.

HARRY GORDON, KISTLER LEATHER CO. LABORATORY.

The "Total Ash" in vegetable tanned leather may be defined as follows: The residue obtained when completely igniting the original sample at a dull red heat.

As I am not familiar with Chrome Leather having never analyzed samples of same, I am not in a position to define the "Total Ash" of a "Chrome Tanned Leather."

ERWIN J. KERN, A. F. GALLUN & SONS CO.

As for what is meant by "total ash", this is purely a matter of definition, and as yet no generally accepted definition exists. There is, of course, a definition for the simple term "ash" which is the residue left after heating to dull redness until all carbonaceous matter is consumed. But, the difficulty confronting the Committee in deciding upon a definition for total ash is that the term could logically be used to indicate two very different things. For example, the ash of the whole leather might be called "total ash". Then again the term might be used to indicate the sum of the ashes of the constituents of the leather when ashed separately. However, it would not be practical, if possible, to separate a leather into each of its constituents for ashing separately; probably the nearest approach would be separation into soluble and insoluble portions.

Let the ash of the whole leather equal a, the ash of the soluble portion equal s, and the ash of the insoluble portion equal i.

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In general *a* may be greater or less than, but rarely equal to, the sum of *s* and *i*. Now it appears to me immaterial what definitions we use so long as we recognize that no specific relation exists between the above quantities and that we cannot calculate one from the other two.

In practice the question of methods of ashing does not bother us, since we always determine the SO_3 and Cl in the leather as well as in the ash and consequently are not led astray by the reduction of sulfates during ashing.

TRAVIS LOWRY, KISTLER LEATHER CO. LABORATORY.

The determination of the "Total Ash" in leather is the incinerating of a portion of the sample in a platinum dish at a dull red heat until all of the carbon is burned off.

F. F. MARSHALL, KISTLER LEATHER CO. LABORATORY.

The writer's understanding of the "Total Ash" in leather is the total residue after burning off all carbon at fixed temperature and under fixed conditions.

V. J. MLEJNEK, GRATON & KNIGHT MANUFACTURING CO.

As we understand it, the object of a total ash on a leather is to obtain a measure of the mineral acids and bases in a form as nearly identical with that in which they are present in the original leather as can conveniently be done.

Of course, it is clearly understood that the mineral matter is not present in the ash in its original form, some of the chlorides, sulphates, etc., being reduced to bases in the process of ashing. Also, that, according to the recent committee work, the total ash figure obtained by the water soluble method gives a value more nearly comparable with the true salt content than the direct ashing.

Still, in view of the fact that neither method gives a true figure for mineral content, and the fact that much more concordant results are obtained in different laboratories by the direct ashing than by the water soluble method, we are prone to favor the direct ashing method for total ash.

Our definition for a total ash in leather would be as follows: The total ash of a leather is the measure of the mineral acids and bases in a form as nearly identical with that in the original leather as can be conveniently obtained, *i. e.* by carefully burning off a weighed portion of the original leather in a platinum dish

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at a low heat until all the carbon has been burned off, cooling and weighing the residue as ash. The same definition applies to both vegetable and chrome tanned leather.

R. E. PORTER, ASHLAND LEATHER COMPANY.

The total ash in leather is the total weight after complete ignition at some definite temperature.

J. S. ROGERS, KISTLER, LESH & COMPANY, LABORATORY.

Total ash in vegetable tanned leather is the residue remaining after carefully and gently burning leather at a dull red heat in access to air until all charcoal and organic matter are burned off. In case of difficulty in burning off all of the carbon at a gentle heat, the residue should be leached out with hot water, filtered, the charcoal and filter burned and combined with the evaporated filtrate and then gently ignited again. The least burning necessary to accomplish this end should be used. It is not necessary to burn the ash to constant weight.

Since the Committee has done no work on Chrome Tanned Leather, I do not feel that we should be called upon to outline a method at the present time, however, I see no reason why the method used for vegetable tanned leather could not also be applied to chrome leather.

Chairman.—It appears that the greater number of the collaborators define the "Total Ash in Leather" as the amount of mineral matter remaining after complete ignition of the leather, and a number mention that the ignition should be made under fixed conditions.

TABULATION OF HYDROGEN AND HYDROXYL ION CONCENTRATIONS OF SOME ACIDS AND BASES.

By Arthur W. Thomas.

Received December 16, 1919.

It has lately been shown in chemical research that the actual concentration of hydrogen ion of an acid solution and of hydroxyl ion of an alkaline solution are of greater significance in most reactions than the total titrable acidity or alkalinity. In the manufacture of leather, most leather chemists concede the rôle of hydrogen and of hydroxyl ions to be of prime importance in the various steps involved in converting hide to leather.

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The reason why hydrogen ion and hydroxyl ion concentrations are not considered more frequently, as such, in discussions on leather chemistry is no doubt due to lack of available figures for the concentrations of these ions for varying strengths of common acids and bases. Consequently strengths of acid or of alkaline solutions are generally given in terms of percentages of the particular acids or bases, which results in the accumulation of a confusing mass of arbitrary figures which do not show any simple relationship one to another. This condition of affairs can be greatly simplified and the action of acid and alkali be better understood if the strengths are expressed in terms of molarity and likewise in terms of the actual concentration of the active parts of the acids or bases, namely, hydrogen or hydroxyl ion as the case may be.

The writer has undertaken to compute and compile such data which are offered herewith for the use of the A. L. C. A.

The hydrogen ion concentrations for concentrations from 0.001 to 2 molar of the following acids are given,—Acetic, Boric, Butyric, Carbonic, Citric, Formic, Gallic, Hydrochloric, Lactic, Nitric, Oxalic, Phosphoric, Salicylic, Sulphuric and Tartaric. Hydroxyl ion concentrations for the same range are given for the following bases,—Ammonium, Barium, Calcium, Potassium and Sodium Hydroxides.

In general two modes of procedure have been used in the calculations. For the weak acids the concentrations of hydrogen ion have been calculated from the ionization constant (determined by conductivity measurements), by means of Ostwald's dilution law,—

$$K = \frac{\alpha^2}{(1-\alpha)V},$$

where K = the ionization (or dissociation) constant.
α = degree of ionization (or dissociation).
V = the volume in which one gram molecular weight of the substance was dissolved.

Solving for α in the above expression we get,—

$$\alpha = \sqrt{KV + \frac{K^2V^2}{4}} - \frac{KV}{2}.$$

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Since $\frac{K^2V^2}{4}$ is a very small number, it can be disregarded, and since we desire to express our results in per cent. ionization, our expression reduces to,—

$$\text{Per cent. ionization} = 100\sqrt{\frac{K}{V}} - \frac{KV}{2}.$$

From the ionization percentages the concentrations in grams per liter of hydrogen ion were calculated.

For the strong acids, the experimentally determined values for 100α at various concentrations (V) were found in the literature. Then the 100α values were plotted against the logarithms of the volumes and a smooth curve drawn through the points. The values for 100α at the concentrations desired, were read from the curve. The concentrations in grams per liter of hydrogen ion were then calculated from the ionization percentages.

The hydroxyl ion concentrations of the bases were obtained in a like manner.

No claim for the absolute accuracy of these figures is made. They may be as much as 5% in error especially in the cases of the strong acids and bases. They are the best obtainable at this time, however, and it is to be borne in mind that they have been arrived at from conductivity data, and not from measurements by the hydrogen electrode.

Acids.

Acetic Acid.—Values calculated from the experimentally determined figures of Kendall[1].

Boric Acid.—Calculated from $K = 6.6 \times 10^{-10}$ at 25° C., by Lundén[2]. 0.8 molar is saturated solution and since this acid is so exceedingly weak, only the concentrations at 0.8, 0.1, 0.01 and 0.001 molar are given in the table.

Butyric Acid.—For concentrations 2.0—0.1 molar, calculated from $K = 1.49 \times 10^{-5}$ at 25° C. by Ostwald[3]. From 0.1 — 0.001 molar calculated from Ostwald's experimental values.

[1] Meddelanden fran K. Vetenskapakadamiens Nobelinstitut, Band 2, Nr. 38, Pages 1–27 (1913).

[2] *J. chim. phys.*, **5**, 574 (1907).

[3] *Z. physik. Chem.*, **3**, 170–197 (1889).

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Carbonic Acid.—The values according to Kendall[4] are given. This acid is so very weak and since its concentration in solution depends upon the pressure over the surface of the solution, that only two significant concentrations are given. These concentrations are given here and not in the table. At 25° C., the solubility of carbon dioxide in water at 1 atmosphere pressure of carbon dioxide is 0.0337 moles per liter. The carbonic acid in this solution is 0.33 per cent. ionized and hence its concentration of hydrogen ion is 0.00011 moles per liter (which is about 0.00011 grams per liter). Under ordinary conditions the partial pressure of carbon dioxide in the air is 3.53×10^{-4} atmosphere at which pressure carbon dioxide is soluble to the extent of 1.19×10^{-5} moles per liter and the ionized portion is 2.05×10^{-6} moles per liter, or the concentration of hydrogen ion is 0.000002 moles (or grams) per liter.

Citric Acid.—For 2.0 — 0.4 molar the values of Kendall, Booge and Andrews[5] are given. From 0.4 — 0.1 molar the values are extrapolated. From 0.01 — 0.001 molar the concentrations are calculated from the measurements of Walden[6].

Formic Acid.—From 2.0 — 0.1 molar the values are calculated from $K = 21.4 \times 10^{-5}$ at 25° C., as given by Ostwald[3]. From 0.1 — 0.001 they are calculated from Ostwald's experimental determinations.

Gallic Acid.—From 1.0 — 0.03 molar are calculated from $K = 4.0 \times 10^{-5}$ as given by Ostwald[7]. From 0.03 — 0.001 molar are calculated from Ostwald's experimental values.

Hydrochloric Acid.—The 2.0 — 0.5 molar figures are from Jones[8]. From 0.5 — 0.001 molar the concentrations are calculated from Kohlrausch's[9] experimentally determined values.

Lactic Acid.—The concentrations 2.0 — 0.1 molar are based upon the figures of Kendall, Booge and Andrews (l. c.). From 0.1 — 0.001 they are calculated from the experimental figures of Ostwald (l. c.).

[4] *J. Am. Chem. Soc.*, **38**, 1481 (1916).
[5] *J. Am. Chem. Soc.*, **39**, 2303-23 (1917).
[6] *Z. physik. Chem.*, **10**, 568 (1892).
[7] *Z. physik. Chem.*, **3**, 241-288 (1889).
[8] Carnegie Institution of Washington, Publication No. 60, page 93 (1907).
[9] Morgan's Elements of Physical Chemistry, 4th Edition, page 519 (1908).

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Nitric Acid.—The 2.0 and 1.0 molar values are taken from Jones (l. c., page 96). From 0.5 — 0.001 molar the values are calculated from Kohlrausch's (l. c.) experimental data.

Oxalic Acid.—For this acid, the only data available are those published by Ostwald (l. c.) which embrace solely the concentrations 0.03 — 0.004 molar. This acid is too highly dissociated to permit calculation of per cent. ionization by the dilution law.

Phosphoric Acid.—Calculation from data of Kendall, Booge and Andrews (l. c.) gave the figures 2.0 — 0.1 molar. From 0.1 — 0.001 the values are based upon the experimental data of Noyes and Eastman[10].

Salicylic Acid.—These values are based upon the experimental data of Kendall (same reference as for Acetic Acid). The highest concentration given for this acid is 0.0167 molar because this is the limit of solubility.

Sulphuric Acid.—The 2.0 and 1.0 molar figures are from Jones (l. c.). From 0.5 — 0.001 the values are calculated from the experimental data of Kohlrausch (l. c.).

Tartaric Acid.—From 2.0 — 0.04 the figures are calculated from the data of Kendall, Booge and Andrews (l. c.). Therefrom to 0.001 molar, they are calculated from the experimental data of Ostwald (l. c.).

BASES.

Ammonium Hydroxide.—The figures for this weak base were calculated by means of the dilution law from $K = 1.8 \times 10^{-5}$ at 25° C., as given by Noyes, Kato and Sosman[11].

Barium Hydroxide.—The only data available for this base are those of Noyes and Eastman (l. c.) page 268, which range from 0.001 — 0.05 molar, upon which my calculations are based.

Calcium Hydroxide.—I have not succeeded in finding any series of experimental data for this base ,but it is so similar to Barium Hydroxide that no great error would be introduced if one used the Barium Hydroxide data for lime.

Potassium Hydroxide.—The 2.0 molar figure is from Jones (l. c. page 48). From 1.0 — 0.4 molar and 0.03 — 0.001 molar,

[10] Carnegie Institution of Washington, Publication No. 63, page 268 (1907).

[11] *Z. physik. Chem.*, 73, 1 (1910).

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the calculations are based on Kohlrausch's (l. c.) data. The values between 0.4 and 0.03 molar are obtained by extrapolation.

Sodium Hydroxide.—The 2.0 molar figure is from Jones (l. c. page 41). The other figures comes from Kohlrausch (l. c.).

It will be noted that the data are given in each case for the temperature 25° C. The temperature coefficient for dissociation is small enough to be neglected for practical purposes, so that it will not introduce a large error if the values be considered valid for the range of temperature met with in the tannery.

Listing the acids in order of their strengths, or in other words in order of their hydrogen ion activities, with the strongest at the top and the weakest at the bottom, we have,

Nitric, Hydrochloric
Sulphuric
Oxalic
Phosphoric
Salicylic
Tartaric
Citric
Formic
Lactic
Gallic
Acetic
Butyric
Carbonic
Boric

The bases in order of their hydroxyl ion activities are,—

Potassium Hydroxide
Sodium Hydroxide
Barium Hydroxide, Calcium Hydroxide
Ammonium Hydroxide

Effect of Added Salts.

The figures given are absolutely true only when the acids or bases are present alone in solution. The addition of salts alters their hydrogen or hydroxyl ion activities. Neutral chlorides tend to increase the hydrogen ion activities of acids [12, 13, 14, 15, 16, 17,

[12] Poma, *Z. physik. Chem.*, **88**, 671 (1914).
[13] Harned, *J. Am. Chem. Soc.*, **37**, 2460 (1915).
[14] Fales and Nelson, *ibid.*, **37**, 2769 (1915).
[15] Thomas and Baldwin, This JOURNAL, **13**, 248 (1918).
[16] Baldwin, This JOURNAL, **14**, 10 (1919).
[17] Thomas and Baldwin, *J. Am. Chem. Soc.*, **41**, 1981 (1919).

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and the hydroxyl ion activities of bases [13]. Neutral sulphates tend to decrease the hydrogen ion activities of acid solutions [15, 16, 17].

DEGREE OF IONIZATION OF ACIDS AT VARIOUS CONCENTRATIONS AT 25° C.

Moles of acid per liter	Hdrochloric acid			Nitric acid		
	Per cent. Ionized	Moles H+ per liter	Grams H+ per liter	Per cent. Ionized	Moles H+ per liter	Grams H+ per liter
2.0	69.3	1.386	1.397	73.9	1.478	1.490
1.0	79.6	0.796	0.802	84.8	0.848	0.855
0.9	81.5	0.734	0.739	—	—	—
0.8	83.3	0.666	0.671	—	—	—
0.7	84.7	0.593	0.598	—	—	—
0.6	86.5	0.519	0.523	—	—	—
0.5	87.5	0.438	0.441	87.9	0.439	0.443
0.4	88.7	0.355	0.358	89.4	0.358	0.360
0.3	90.1	0.270	0.272	90.7	0.272	0.274
0.2	92.0	0.184	0.186	92.9	0.186	0.188
0.10	94.8	0.095	0.096	96.0	0.096	0.097
0.09	95.2	0.086	0.086	96.3	0.087	0.087
0.08	95.6	0.076	0.077	96.8	0.077	0.078
0.07	95.8	0.067	0.068	97.3	0.068	0.069
0.06	96.4	0.058	0.058	97.6	0.059	0.059
0.05	96.8	0.048	0.049	98.3	0.049	0.050
0.04	97.6	0.039	0.039	98.7	0.039	0.040
0.03	98.0	0.029	0.030	99.2	0.030	0.030
0.02	98.8	0.020	0.020	99.3	0.020	0.020
0.010	99.8	0.0100	0.0101	99.3	0.0099	0.0100
0.009	99.9	0.0090	0.0091	99.3	0.0089	0.0090
0.008	100.0	0.0080	0.0081	99.3	0.0079	0.0080
0.007	100.0	0.0070	0.0071	99.3	0.0070	0.0070
0.006	100.0	0.0060	0.0060	99.4	0.0060	0.0060
0.005	100.0	0.0050	0.0050	99.4	0.0050	0.0050
0.004	100.0	0.0040	0.0040	99.4	0.0040	0.0040
0.003	100.0	0.0030	0.0030	99.5	0.0030	0.0030
0.002	100.0	0.0020	0.0020	99.5	0.0020	0.0020
0.001	100.0	0.0010	0.0010	100.0	0.0010	0.0010

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DEGREE OF IONIZATION OF ACIDS AT VARIOUS CONCENTRATIONS AT 25° C.

Moles of acid per liter	Sulphuric acid			Phosphoric acid		
	[1]Per cent. Ionized	Moles H+ per liter	Grams H+ per liter	[2]Per cent. Ionized	Moles H+ per liter	Grams H+ per liter
2.0	39.9	1.596	1.609	16.1	0.322	0.325
1.0	50.7	1.014	1.022	17.5	0.175	0.177
0.9	50.9	0.916	0.923	17.7	0.159	0.161
0.8	51.4	0.822	0.829	17.9	0.143	0.144
0.7	52.0	0.728	0.835	18.0	0.126	0.127
0.6	52.9	0.635	0.640	18.8	0.113	0.114
0.5	53.6	0.536	0.540	19.0	0.095	0.096
0.4	54.7	0.438	0.442	19.8	0.079	0.080
0.3	56.0	0.336	0.339	20.7	0.062	0.063
0.2	57.6	0.230	0.232	22.8	0.046	0.046
0.10	60.7	0.121	0.122	27.5	0.028	0.028
0.09	61.1	0.110	0.111	28.5	0.026	0.026
0.08	61.7	0.099	0.100	30.0	0.024	0.024
0.07	62.4	0.087	0.088	31.0	0.022	0.022
0.06	63.5	0.076	0.077	33.0	0.020	0.020
0.05	64.8	0.065	0.065	35.0	0.018	0.018
0.04	66.8	0.053	0.054	38.0	0.015	0.015
0.03	69.4	0.042	0.042	42.0	0.013	0.013
0.02	73.1	0.029	0.029	47.5	0.010	0.010
0.010	79.6	0.0159	0.0160	59.0	0.0059	0.0059
0.009	80.5	0.0145	0.0146	60.5	0.0054	0.0055
0.008	81.8	0.0131	0.0132	63.0	0.0050	0.0051
0.007	82.7	0.0116	0.0117	65.0	0.0046	0.0046
0.006	84.2	0.0101	0.0102	67.5	0.0041	0.0041
0.005	85.9	0.0086	0.0087	70.0	0.0035	0.0035
0.004	88.0	0.0070	0.0071	73.5	0.0029	0.0030
0.003	90.5	0.0054	0.0055	77.5	0.0023	0.0023
0.002	94.7	0.0038	0.0038	83.0	0.0017	0.0017
0.001	97.7	0.0020	0.0020	89.0	0.0009	0.0009

[1] 100 per cent. ionization taken as complete ionization into H+, H+, and SO''_4.
[2] 100 per cent. ionization taken as complete ionization into H+ and $H_2PO'_4$.

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DEGREE OF IONIZATION OF ACIDS AT VARIOUS CONCENTRATIONS AT 25° C.

Moles of acid per liter	Formic acid			Acetic acid		
	Per cent. Ionized	Moles H+ per liter	Grams H+ per liter	Per cent. Ionized	Moles H+ per liter	Grams H+ per liter
2.0	1.03	0.0206	0.0208	0.30	0.00600	0.00605
1.0	1.5	0.0150	0.0151	0.37	0.00370	0.00373
0.9	1.6	0.0144	0.0145	0.40	0.00360	0.00363
0.8	1.7	0.0136	0.0137	0.42	0.00336	0.00339
0.7	1.8	0.0126	0.0127	0.45	0.00315	0.00318
0.6	1.9	0.0114	0.0115	0.50	0.00300	0.00302
0.5	2.1	0.0105	0.0106	0.57	0.00285	0.00287
0.4	2.3	0.0092	0.0093	0.6	0.00240	0.00242
0.3	2.6	0.0078	0.0079	0.7	0.00210	0.00212
0.2	3.2	0.0064	0.0065	0.9	0.00180	0.00181
0.10	4.5	0.0045	0.0045	1.3	0.00130	0.00131
0.09	4.7	0.0042	0.0042	1.4	0.00126	0.00127
0.08	5.0	0.0040	0.0040	1.5	0.00120	0.00121
0.07	5.4	0.0038	0.0038	1.55	0.00109	0.00110
0.06	5.8	0.0035	0.0035	1.7	0.00102	0.00103
0.05	6.4	0.0032	0.0032	1.9	0.00095	0.00096
0.04	7.1	0.0028	0.0028	2.1	0.00084	0.00085
0.03	8.1	0.0024	0.0024	2.4	0.00072	0.00073
0.02	9.7	0.0019	0.0019	3.0	0.00060	0.00060
0.010	13.4	0.00134	0.00135	4.2	0.00042	0.00042
0.009	14.0	0.00126	0.00127	4.4	0.00040	0.00040
0.008	14.8	0.00118	0.00119	4.7	0.00038	0.00038
0.007	15.5	0.00109	0.00110	5.0	0.00035	0.00035
0.006	16.6	0.00100	0.00101	5.4	0.00032	0.00033
0.005	18.0	0.00090	0.00091	5.9	0.00030	0.00030
0.004	20.1	0.00080	0.00081	6.6	0.00026	0.00027
0.003	22.0	0.00066	0.00067	7.5	0.00023	0.00023
0.002	27.1	0.00054	0.00055	9.2	0.00018	0.00019
0.001	35.8	0.00036	0.00036	12.8	0.00013	0.00013

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DEGREE OF IONIZATION OF ACIDS AT VARIOUS CONCENTRATIONS AT 25° C.

Moles of acid per liter	Gallic acid			Lactic acid		
	Per cent. Ionized	Moles H+ per liter	Grams H+ per liter	Per cent. Ionized	Moles H+ per liter	Grams H+ per liter
2.0	—	—	—	0.8	0.0160	0.0161
1.0	0.63	0.0063	0.0064	1.1	0.0110	0.0111
0.9	0.68	0.0061	0.0062	1.2	0.0108	0.0109
0.8	0.70	0.0056	0.0056	1.3	0.0104	0.0105
0.7	0.74	0.0052	0.0052	1.4	0.0098	0.0099
0.6	0.80	0.0048	0.0048	1.5	0.0090	0.0091
0.5	0.89	0.0045	0.0045	1.6	0.0080	0.0081
0.4	1.00	0.0040	0.0040	1.8	0.0072	0.0073
0.3	1.15	0.0035	0.0035	2.2	0.0066	0.0066
0.2	1.40	0.0028	0.0028	2.7	0.0054	0.0054
0.10	1.98	0.00198	0.00200	3.7	0.00370	0.00373
0.09	2.05	0.00185	0.00186	3.8	0.00342	0.00345
0.08	2.20	0.00176	0.00177	4.1	0.00328	0.00331
0.07	2.30	0.00161	0.00162	4.3	0.00301	0.00303
0.06	2.50	0.00150	0.00151	4.8	0.00288	0.00290
0.05	2.70	0.00135	0.00136	5.2	0.00260	0.00262
0.04	3.0	0.00120	0.00121	5.8	0.00232	0.00234
0.03	3.3	0.00099	0.00100	6.6	0.00198	0.00200
0.02	4.1	0.00082	0.00083	8.0	0.00160	0.00161
0.010	5.9	0.00059	0.00059	11.0	0.00110	0.00111
0.009	6.2	0.00056	0.00056	11.5	0.00104	0.00104
0.008	6.7	0.00054	0.00054	12.2	0.00098	0.00098
0.007	7.0	0.00049	0.00049	12.9	0.00090	0.00091
0.006	7.6	0.00046	0.00046	13.9	0.00083	0.00084
0.005	8.4	0.00042	0.00042	15.1	0.00076	0.00076
0.004	9.3	0.00037	0.00037	16.7	0.00067	0.00067
0.003	10.7	0.00032	0.00032	18.7	0.00056	0.00057
0.002	13.4	0.00027	0.00027	23.0	0.00046	0.00046
0.001	18.7	0.00019	0.00019	30.9	0.00031	0.00031

DEGREE OF IONIZATION OF ACIDS AT VARIOUS CONCENTRATIONS AT 25° C.

Moles of acid per liter	Butyric acid			Boric acid		
	Per cent. Ionized	Moles H+ per liter	Grams H+ per liter	[1]Per cent. Ionized	Moles H+ per liter	Grams H+ per liter
2.0	0.27	0.00540	0.00544	—	—	—
1.0	0.39	0.00390	0.00393	—	—	—
0.9	0.40	0.00360	0.00363	—	—	—
0.8	0.41	0.00328	0.00331	0.003	0.0000240	0.000024
0.7	0.43	0.00301	0.00303	—	—	—
0.6	0.49	0.00294	0.00296	—	—	—
0.5	0.54	0.00270	0.00272	—	—	—
0.4	0.60	0.00240	0.00242	—	—	—
0.3	0.70	0.00210	0.00212	—	—	—
0.2	0.86	0.00172	0.00173	—	—	—

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0.10	1.2	0.00120	0.00121	0.008	0.0000080	0.0000081
0.09	1.25	0.00113	0.00113	—	—	—
0.08	1.35	0.00108	0.00109	—	—	—
0.07	1.4	0.00098	0.00099	—	—	—
0.06	1.6	0.00096	0.00097	—	—	—
0.05	1.7	0.00085	0.00086	—	—	—
0.04	1.95	0.00078	0.00079	—	—	—
0.03	2.2	0.00066	0.00067	—	—	—
0.02	2.7	0.00054	0.00054	—	—	—
0.010	3.8	0.00038	0.00038	0.026	0.0000026	0.0000026
0.009	3.95	0.00036	0.00036	—	—	—
0.008	4.3	0.00034	0.00035	—	—	—
0.007	4.55	0.00032	0.00032	—	—	—
0.006	4.9	0.00029	0.00030	—	—	—
0.005	5.4	0.00027	0.00027	—	—	—
0.004	6.0	0.00024	0.00024	—	—	—
0.003	6.8	0.00020	0.00021	—	—	—
0.002	8.3	0.00017	0.00017	—	—	—
0.001	11.4	0.00011	0.00011	0.080	0.0000008	0.0000008

[1] 100 per cent. ionization taken as complete ionization into $H+$ and H_2BO_3.

DEGREE OF IONIZATION OF ACIDS AT VARIOUS CONCENTRATIONS AT 25° C.

Moles of acid per liter	Oxalic acid			Salicylic acid		
	[1]Per cent. Ionized	Moles H+ per liter	Grams H+ per liter	[2]Per cent. Ionized	Moles H+ per liter	Grams H+ per liter
0.03	73.5	0.0221	0.0223	—	—	—
0.02	79.0	0.0158	0.0159	—	—	—
0.0167	—	—	—	24.0	0.0040	0.0040
0.010	87.0	0.0087	0.0088	27.7	0.0028	0.0028
0.009	88.0	0.0079	0.0080	29.0	0.0026	0.0026
0.008	89.0	0.0071	0.0072	30.5	0.0024	0.0025
0.007	90.0	0.0063	0.0064	32.0	0.0022	0.0023
0.006	91.5	0.0055	0.0055	34.5	0.0021	0.0021
0.005	93.0	0.0047	0.0047	37.0	0.0019	0.0019
0.004	95.0	0.0038	0.0038	40.0	0.0016	0.0016
0.003	—	—	—	44.5	0.0013	0.0013
0.002	—	—	—	51.0	0.0010	0.0010
0.001	—	—	—	62.0	0.0006	0.0006

[1] 100 per cent. ionization taken as complete ionization into $H+$ and HC_2O_4.

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DEGREE OF IONIZATION OF ACIDS AT VARIOUS CONCENTRATIONS AT 25° C.

Moles of acid per liter	Tartaric acid			Citric acid		
	[1]Per cent. Ionized	Moles H+ per liter	Grams H+ per liter	[2]Per cent. Ionized	Moles H+ per liter	Grams H+ per liter
2.0	2.1	0.042	0.042	1.8	0.036	0.036
1.0	2.9	0.029	0.029	2.7	0.027	0.027
0.9	3.0	0.027	0.027	2.8	0.025	0.025
0.8	3.2	0.026	0.026	2.9	0.023	0.023
0.7	3.5	0.025	0.025	3.0	0.021	0.021
0.6	3.7	0.022	0.022	3.1	0.019	0.019
0.5	4.2	0.021	0.021	3.5	0.018	0.018
0.4	4.9	0.020	0.020	4.0	0.016	0.016
0.3	5.7	0.017	0.017	4.7	0.014	0.014
0.2	7.1	0.014	0.014	6.1	0.012	0.012
0.10	9.9	0.0099	0.0100	9.1	0.0091	0.0092
0.09	10.2	0.0092	0.0093	9.5	0.0086	0.0086
0.08	10.9	0.0087	0.0088	10.1	0.0081	0.0081
0.07	11.4	0.0080	0.0081	10.7	0.0075	0.0076
0.06	12.2	0.0073	0.0074	11.5	0.0069	0.0070
0.05	13.1	0.0066	0.0066	12.5	0.0063	0.0063
0.04	14.5	0.0058	0.0058	13.8	0.0055	0.0056
0.03	16.5	0.0050	0.0050	15.5	0.0047	0.0047
0.02	19.5	0.0039	0.0039	18.3	0.0037	0.0037
0.010	27.0	0.0027	0.0027	25.0	0.0025	0.0025
0.009	28.0	0.0025	0.0025	25.9	0.0023	0.0024
0.008	30.0	0.0024	0.0024	27.6	0.0022	0.0022
0.007	31.0	0.0022	0.0022	28.9	0.0020	0.0020
0.006	33.0	0.0020	0.0020	30.8	0.0018	0.0019
0.005	35.5	0.0018	0.0018	33.1	0.0017	0.0017
0.004	39.0	0.0016	0.0016	36.0	0.0014	0.0015
0.003	43.0	0.0013	0.0013	39.8	0.0012	0.0012
0.002	51.0	0.0010	0.0010	47.4	0.0009	0.0010
0.001	65.3	0.0007	0.0007	60.2	0.0006	0.0006

[1] 100 per cent. ionization taken as complete ionization into H+ and $HC_4H_4O'_6$.
[2] 100 per cent. ionization taken as complete ionization into H+ and $H_2C_6H_5O'_7$.

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DEGREE OF IONIZATION OF BASES AT VARIOUS CONCENTRATIONS AT 25° C.

Moles of base per liter	Potassium hydroxide			Sodium hydroxide		
	Per cent. Ionized	Moles OH' per liter	Grams OH' per liter	Per cent. Ionized	Moles OH' per liter	Grams OH' per liter
2.0	66.3	1.326	22.553	57.0	1.140	19.389
1.0	81.9	0.819	13.931	76.6	0.766	13.028
0.9	82.8	0.745	12.674	77.7	0.699	11.894
0.8	84.3	0.759	11.470	79.2	0.634	10.776
0.7	85.0	0.595	10.120	80.4	0.563	9.572
0.6	86.3	0.518	8.807	81.9	0.491	8.358
0.5	87.6	0.438	7.450	83.5	0.418	7.101
0.4	88.8	0.355	6.041	85.3	0.341	5.823
0.3	90.1	0.270	4.600	87.0	0.261	4.439
0.2	92.2	0.184	3.137	89.8	0.180	3.055
0.10	95.0	0.095	1.616	92.9	0.093	1.580
0.09	95.3	0.086	1.459	93.2	0.084	1.427
0.08	95.8	0.077	1.304	93.7	0.075	1.275
0.07	96.2	0.067	1.145	94.1	0.066	1.120
0.06	96.7	0.058	0.987	94.7	0.057	0.966
0.05	97.3	0.049	0.827	95.3	0.048	0.810
0.04	97.9	0.039	0.666	96.0	0.038	0.653
0.03	98.7	0.030	0.504	96.8	0.029	0.494
0.02	99.3	0.020	0.338	97.9	0.020	0.333
0.010	99.9	0.010	0.170	99.5	0.010	0.169
0.009	99.9	0.009	0.153	99.7	0.009	0.153
0.008	100.0	0.008	0.136	99.9	0.008	0.137
0.007	100.0	0.007	0.119	100.0	0.007	0.119
0.006	100.0	0.006	0.102	100.0	0.006	0.102
0.005	100.0	0.005	0.085	100.0	0.005	0.085
0.004	100.0	0.004	0.068	100.0	0.004	0.068
0.003	100.0	0.003	0.051	100.0	0.003	0.051
0.002	100.0	0.002	0.034	100.0	0.002	0.034
0,001	100.0	0.001	0.017	100.0	0.001	0.017

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DEGREE OF IONIZATION OF BASES AT VARIOUS CONCENTRATIONS AT 25° C.

Moles of base per liter	Ammonium hydroxide			Barium Hydroxide		
	Per cent. Ionized	Moles OH' per liter	Grams OH' per liter	[1]Per cent. Ionized	Moles OH' per liter	Grams OH' per liter
2.0	0.30	0.0060	0.1020	—	—	—
1.0	0.42	0.00420	0.0714	—	—	—
0.9	0.45	0.00405	0.0689	—	—	—
0.8	0.47	0.00376	0.0640	—	—	—
0.7	0.50	0.00350	0.0596	—	—	—
0.6	0.55	0.00330	0.0561	—	—	—
0.5	0.60	0.00300	0.0510	—	—	—
0.4	0.67	0.00268	0.0456	—	—	—
0.3	0.77	0.00231	0.0393	—	—	—
0.2	0.94	0.00188	0.0320	—	—	—
0.10	1.33	0.00133	0.0226	—	—	—
0.09	1.40	0.00126	0.0214	—	—	—
0.08	1.49	0.00119	0.0203	—	—	—
0.07	1.59	0.00111	0.0189	—	—	—
0.06	1.72	0.00103	0.0175	—	—	—
0.05	1.88	0.00094	0.0160	80.0	0.040	0.680
0.04	2.12	0.00085	0.0144	81.0	0.032	0.551
0.03	2.42	0.00073	0.0123	82.8	0.025	0.422
0.02	2.96	0.00059	0.0101	86.0	0.017	0.293
0.010	4.15	0.00042	0.0071	88.4	0.009	0.150
0.009	4.37	0.00039	0.0067	90.0	0.008	0.138
0.008	4.62	0.00037	0.0063	90.5	0.007	0.123
0.007	4.93	0.00035	0.0059	91.0	0.006	0.108
0.006	5.33	0.00032	0.0054	91.3	0.0055	0.093
0.005	5.82	0.00029	0.0049	92.0	0.0046	0.078
0.004	6.48	0.00026	0.0044	93.0	0.0037	0.063
0.003	7.44	0.00022	0.0038	94.0	0.0028	0.048
0.002	8.99	0.00018	0.0031	95.0	0.0019	0.032
0.001	12.52	0.00013	0.0021	96.0	0.0010	0.016

[1] 100 per cent. ionization taken as complete ionization into $BaOH^+$ and OH'.

NOTE: If hydroxyl ion concentrations of Calcium Hydroxide solutions be required, it is suggested that the Barium Hydroxide figures be used.

The author expresses his indebtedness to the Messrs. A. F. Gallun and Sons Company, of Milwaukee, who have kindly borne the expense of this compilation, and to Mr. John Arthur Wilson for his criticism of the manuscript.

COLUMBIA UNIVERSITY,
NEW YORK CITY.

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THE TIME FACTOR IN THE ADSORPTION OF THE CONSTITUENTS OF CHROME LIQUOR BY HIDE SUBSTANCE.

By A. W. Thomas, M. E. Baldwin and M. W. Kelly.

Received January 8, 1920.

The concentration factor, that is, the effect of the concentration of a chrome liquor upon the adsorption of its constituents by hide substance was studied by one of us[1] and published last year. It was found at that time that the maximum amount of chromic oxide adsorbable by hide substance from a given liquor was 134 mg. per 1 gram of hide substance, corresponding to a "tetrachrome" leather. This maximum adsorption was obtained by soaking 5 gm. of hide powder in 200 cc. of a chrome liquor containing 1.675 gm. Cr_2O_3 per 100 cc. of liquor. The time of contact of hide powder and chrome liquor was arbitrarily set at two days. The object of our further study as published in part at this time is to show the effect of time on adsorption.

Materials Used.

Chrome Liquor.—The chrome liquor used was a stock liquor diluted with distilled water so as to have a concentration of approximately 1.675 gm. of Cr_2O_3 per 100 cc. The stock chrome liquor was of the following composition,—

	Gm. per liter
Cr_2O_3	215.0
SO_3	219.0
Fe_2O_3	30.9
Al_2O_3	3.2
NaCl	6.5
Glucose	none
Sp. G.	1.625 at 27° C.

Basicity corresponding to Cr(OH) 1.06, (SO_4) 0.97.

169.3 cc. of this stock liquor were diluted to 2200 cc. before using. This diluted liquor showed upon analysis,—

[1] Mabel E. Baldwin, The Effect of the Concentration of a Chrome Liquor upon Adsorption by Hide Substance. This Journal, 14, 433 (1919).

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	Gm. per 100 cc.
Cr_2O_3	1.698
SO_3	1.628

HIDE POWDER (*American Standard*).

	Per cent.
Moisture	14.22
Ash	0.24
Protein (N x 5.614)	86.45

PROCEDURE.

Two hundred cc. portions of the diluted chrome liquor were poured upon 5 gm. portions of hide powder in each of ten glass-stoppered bottles. These mixtures were kept at room temperature (about 26° C.), agitated frequently, and filtered off at definite intervals,—1, 2, 4, 6, 8, 12, 24, 48, 72, and 96 hours. They were filtered by suction on a dry paper in a Buchner funnel, the filtrate set aside for analysis and the chromed hide powder was then washed with 500 cc. of water which removed all the chrome liquor not chemically combined.

The washed chromed hide powder was partially dried at 40° C., and completed at 100° C., to the water-free condition.

The filtered liquor was analyzed for hydrogen ion concentration (immediately after filtration), Cr_2O_3 and Total Acidity. The chromed hide powder was analyzed for Protein, Ash, Cr_2O_3 and SO_3. The methods used are indicated in the paper lately published by Miss Baldwin (loc. cit.).

Measurements of the hydrogen ion concentrations of the filtered liquors were made immediately because it has previously been shown[1] that a slow hydrolytic change takes place in chrome liquors after dilution resulting in appreciable changes in hydrogen ion concentration. To exclude the possibility of attributing changes of this kind to adsorption by the hide substance, a parallel set of measurements upon a portion of the diluted chrome liquors at the intervals of 1, 2, 4, 6, 8, 12, 24, 48, 72 and 96 hours was made. Any differences between the two curves are due to adsorption of acid by the hide substance.

RESULTS.

The analyses of the dried chromed hide substance for each time interval are given in Table I. The analyses of the filtrates are to be found in Table II.

[1] Thomas and Baldwin, This JOURNAL, 13, 248 (1918).

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TABLE I.—THE COMPOSITION OF CHROMED HIDE SUBSTANCE AFTER VARIOUS LENGTHS OF TIME OF CONTACT WITH CHROME LIQUOR.

Time of contact	Protein per cent.	Cr_2O_3 per cent.	SO_3 per cent.	Ash per cent.
1 hour	87.46	3.52	5.55	5.09
2	85.33	5.61	6.28	6.40
4	81.80	6.94	6.85	7.80
6	80.17	7.72	7.58	8.57
8	78.71	8.03	7.73	9.31
12	77.14	8.56	8.46	10.06
24	76.07	—	9.21	11.10
48	74.89	10.41	9.91	11.80
72	73.26	10.77	9.90	12.34
96	71.63	11.01	9.96	12.90

TABLE II.—THE COMPOSITION OF LIQUORS[1] AFTER VARIOUS LENGTHS OF TIME OF CONTACT WITH HIDE SUBSTANCE.

Liquor	Total acidity as gm. SO_3 per 200 cc.	Cr_2O_3 gm. per 200 cc.	Concentration of H+ ion in moles per liter of filtrate	Concentration of H+ ion in moles per liter in control liquor
0 hour	—	—	0.000631	0.000631
1	3.040	3.199	0.000646	0.000912
2	2.952	3.124	0.000724	0.000955
4	2.902	3.053	0.000692	0.000741
6	2.865	2.993	0.000646	0.000692
8	2.861	2.965	0.000631	0.000631
12	2.853	2.930	0.000603	0.000575
24	2.832	—	0.000549	0.000549
48	2.805	2.804	0.000524	0.000537
72	2.805	2.742	0.000562	0.000646
96	2.805	2.711	0.000617	0.000724

[1] An aliquot of the filtrate was taken for analysis in each case and calculated to 200 cc. of liquor, assuming (not correct, of course) that concentration was unaltered by contact with chromed hide substance.

The changes in hydrogen ion centrations can be studied better by means of Figure 1.

The analytical figures shown in Tables I and II served as bases of calculation for the results given in the tables and graphs which follow.

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Figure 1

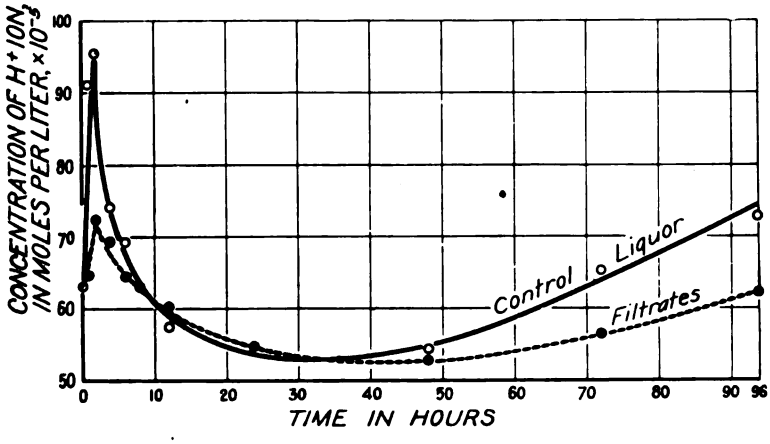

TABLE III.—Amounts of Chromic Oxide Adsorbed by Unit Weight of Hide Substance.

Milligrams adsorbed by 1 gram of hide substance.

	Calculated from analysis of powder		Calculated from analysis of filtrate	
	Cr_2O_3	Cr+++	Cr_2O_3	Cr+++
1 hour	33.7	23.1	(39.6)	(27.1)
2	65.6	44.9	54.6	37.4
4	84.6	57.9	68.8	47.1
6	96.0	65.7	80.8	55.3
8	101.7	69.6	86.4	59.1
12	110.7	75.7	93.4	63.9
24	133.6	91.4	—	—
48	138.6	94.8	118.6	81.1
72	146.6	100.3	131.0	89.6
96	153.3	104.9	137.2	93.9

TABLE IV.—Amounts of Sulphuric Acid Adsorbed by Unit Weight of Hide Substance.

Milligrams adsorbed by 1 gram of hide substance.

	Calculated from analysis of powder		Calculated from analysis of filtrate	
	SO_3	SO_4	SO_3	SO_4
1 hour	63.3	76.0	43.0	51.6
2	71.0	85.2	60.6	72.7
4	83.5	100.2	70.6	84.8
6	94.3	113.2	78.0	93.6
8	97.9	117.5	78.8	94.6
12	109.4	131.3	80.4	96.5
24	120.7	144.8	84.6	101.5
48	131.9	158.3	90.0	108.0
72	134.8	161.8	90.0	108.0
96	138.7	166.4	90.0	108.0

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The relations between the figures given in the above tables are perhaps more clearly shown by the graphs in Figures 2 and 3.

Figure 2

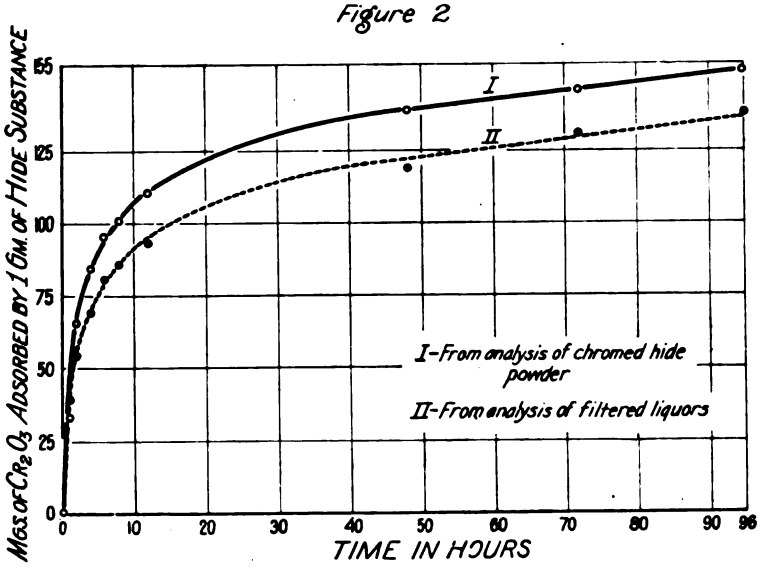
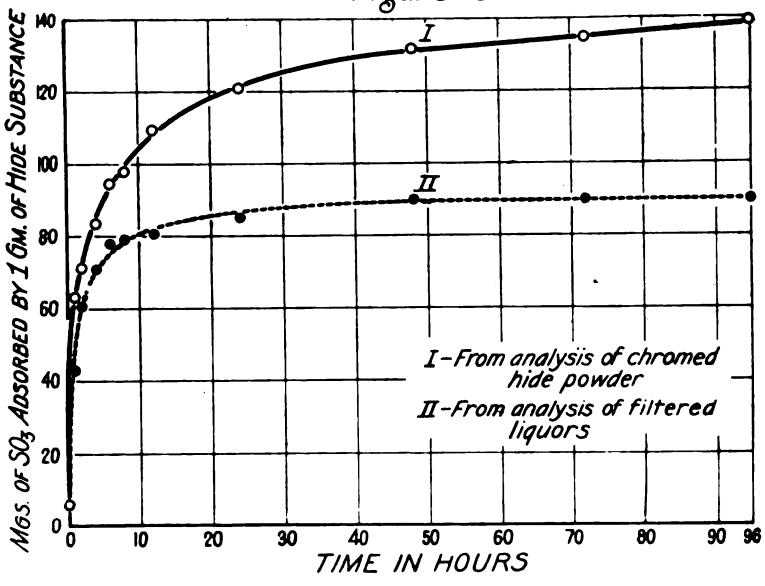


Figure 3



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Examination of Figures 2 and 3 shows quite strikingly that there is a wide difference in results based on the chromed hide substance analyses as compared with those based upon analyses of the liquors filtered off from the various portions of chromed hide substance. This point has been discussed in an earlier paper (Miss Baldwin, Loc. Cit.). The discrepancy between the two sets of figures is due to the fact that as the hide substance adsorbs Cr_2O_3, $SO_4^=$ and H^+, it imbibes water from the chrome liquor as well, and as J. A. and W. H. Wilson[1] have demonstrated, the concentration of the inner solution, held within the network of the collagen molecules, must be less than that of the main body of liquid, or the outer solution.

It is not strictly correct to say that the collagen imbibes water from the chrome liquor. It really imbibes a more dilute chrome liquor, but since the surfaces of the hide fibers are bathed with the outer liquid, i. e., the concentrated chrome liquor, it is obviously impossible to separate the two in order to make an analytical differentiation, hence for the calculations which follow we shall consider the inner solution to be water with the inevitable error brought in by this assumption. Provided one does not exceed a hydrogen ion concentration of approximately 0.005 moles per liter the amounts of imbibed water ought to increase with increase in hydrogen ion concentration[2] and consequently the discrepancy between the Cr_2O_3 adsorbed by hide substance as calculated from the analysis of the filtered liquor compared with that actually found in the chromed hide substance should be greater with higher hydrogen ion concentrations.

We have calculated the ratios of milligrams of Cr_2O_3 adsorbed by 1 gram of hide substance, calculated from analysis of the liquor filtered off, to milligrams of Cr_2O_3 adsorbed by 1 gram of hide substance, calculated from analysis of the chromed hide substance. These figures are submitted in Table V.

It will be seen from the ratios given below that the greatest deviation is found with the 2, 4 and 6 hour specimens. Comparing these with the hydrogen ion values (Figure 1), it is noted that these specimens were bathed in solutions of higher hydrogen ion concentrations than the 8, 12, 24, 48, 72 and 96 hour specimens, and our previously made assumption is checked.

[1] *J. Am. Chem. Soc.*, **40**, 886 (1918).

[2] H. R. Procter, *Trans. Chem. Soc.*, **105**, 317 (1914).

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TABLE V.—RATIO OF ADSORBED CHROMIC OXIDE CALCULATED FROM LIQUOR FILTERED OFF TO THAT CALCULATED FROM CHROMED HIDE SUBSTANCE, AND AMOUNTS OF IMBIBED WATER.

Time	Ratio	Cc. of "water" imbibed by 5 gm. hide substance is greater than,—
1 hour	.—[1]	—
2	0.83	34
4	0.81	38
6	0.84	32
8	0.85	30
12	0.84	32
24	—[1]	—
48	0.86	28
72	0.90	20
96	0.90	20

[1] Analytical figures in error.

It is possible to calculate the minimal amount of water or rather dilute inner solution, imbibed by the hide substance from the ratios given, e. g., for the 2 hour case, the ratio is 0.83. The volume of the chrome liquor was initially 200 cc. Hence the volume after adsorption and imbibition by the hide substance was $200 \times 0.83 = 166$ cc. Therefore at least 34 cc. of water was imbibed by the chromed collagen. The rest of the values so calculated are given in Table V.

Similar reasoning applies to the discrepancy in the SO_3 values although the amounts of water imbibed may not be accurately calculated due to the fact that the SO_3 adsorbed calculated from the analyses of the filtered liquors is based upon the assumption that the acidity of the chrome liquor is due to sulphuric acid, which is not apt to be strictly true. We intend to report in detail upon this subject in a later publication.

The figures given in the ensuing tables are based upon calculations from the analysis of the chromed hide substance.

As stated earlier in this paper, our object was to determine the speed of adsorption and the time for maximum adsorption, using a liquor whose concentration was found to give the maximum value (M. E. Baldwin, loc. cit.). We believed that the reaction would approach its limit at 96 hours, but erred in our guess as is evidenced by Figure 2. At 96 hours the slope is still upward. The limiting value will be determined and reported in a later communication.

To get an idea of the relative amounts of chromic oxide and sulphuric acid adsorbed at each interval of time, Tables VI and VII are submitted.

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TABLE VI.—Relative Amounts of Cr_2O_3 and of SO_3 Adsorbed at Each Interval, in Terms of Per Cent. of Total at End of 96 Hours.

Hours	Cr_2O_3	SO_3
1	22.0%	45.6%
2	42.8	51.2
4	55.2	60.2
6	62.6	68.0
8	66.4	70.6
12	72.2	78.9
24	87.1	87.0
48	90.4	95.1
72	95.6	97.2
96	100.0	100.0

TABLE VII.—Relative Amounts of Cr_2O_3 and of SO_3 Adsorbed as Per Cent. of Total Amount of Both at End of Each Interval.

Hours	Cr_2O_3 per cent.	SO_3 per cent.	Ratio of equivalents Cr_2O_3 : SO_3
1	34.7	65.3	1 : 3.56
2	48.0	52.0	1 : 2.05
4	50.3	49.7	1 : 1.88
6	50.4	49.6	1 : 1.86
8	51.0	49.0	1 : 1.82
12	50.3	49.7	1 : 1.88
24	—	—	—
48	51.2	48.8	1 : 1.80
72	52.1	47.9	1 : 1.75
96	52.5	47.5	1 : 1.73

It is interesting to note that in the two hour adsorption the ratio of equivalents of Cr_2O_3 and of SO_3 combined with hide substance is almost exactly 1 Cr_2O_3, 2 SO_3 which corresponds with $Cr(OH)SO_4$, and this is identical with the composition of the original liquor.

A fact well known to leather chemists is that during chrome tannage the acidity of the liquor increases. This point is brought out in the above table i. e., the number of equivalents of SO_3 combined with the hide substance, compared to one equivalent of Cr_2O_3, rapidly decreases as time of tannage increases, or in other words the ratio of SO_3 to Cr_2O_3 in the liquor becomes greater with time of tannage.

Tables VI and VII indicated that the speed of adsorption of SO_3 was considerably greater during the initial periods than later and that suggested testing the speed of reaction by means of the

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well known reaction speed formulae. The speed does not follow either the mono-, bi- or trimolecular reaction formulae, but the "constants" calculated by means of the monomolecular reaction law,—

$$K = \frac{1}{t} \log \frac{a}{a-x}$$

where t = time
a = initial concentration
x = amount adsorbed in time t

show an interesting relation between Cr_2O_3 and SO_3.

TABLE VIII.—Reaction of Hide Substance With Cr_2O_3 of Chrome Liquor.

$a = 679.4$ mg. Cr_2O_3.

t (in hours)	x (Cr_2O_3 combined) mg.	$(a-x)$ mg.	$K = \frac{1}{t} \log \frac{a}{a-x}$
1	33.7	645.7	0.02210
2	65.6	613.8	0.02205
4	84.6	594.8	0.01444
6	96.0	583.4	0.01103
8	101.7	577.1	0.00880
12	110.7	568.7	0.00644
24	133.6	545.8	0.00396
48	138.6	540.8	0.00206
72	146.6	532.8	0.00146
96	153.3	526.1	0.00116

TABLE IX.—Reaction of Hide Substance With Sulphuric Acid of Chrome Liquor.

$a = 651.0$ mg. SO_3

t (in hours)	x (SO_3 combined) mg.	$(a-x)$ mg.	$K = \frac{1}{t} \log \frac{a}{a-x}$
1	63.3	587.7	0.04442
2	71.0	580.0	0.02508
4	83.5	567.5	0.01490
6	94.3	556.7	0.01133
8	97.9	553.1	0.00885
12	109.4	541.6	0.00666
24	120.7	530.3	0.00371
48	131.9	519.1	0.00205
72	134.8	516.2	0.00140
96	138.7	512.3	0.00108

Comparison of the speed of reaction constant, K, in the tables above shows that at the end of one hour, sulphuric acid has com-

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bined with hide substance just twice as fast as chromic oxide, but that the speeds of combination are practically identical after two hours contact of hide substance and the chrome liquor.

We are greatly indebted to the Messrs. A. F. Gallun and Sons Company of Milwaukee for their generous support of this research.

LABORATORY OF COLLOID CHEMISTRY,
COLUMBIA UNIVERSITY,
NEW YORK CITY.

SYNTHETIC TANNINS AND THEIR USE IN THE TANNERY.

By Professor E. Nihoul.

(Translated from *Chimie et Industrie* 11, 1024 (1919).)

Classification and Constitution of the Tannins.—Trimble's generally accepted classification divides the tannins into two groups, pyrogallol and catechol. *Pyrogallol Tannins*: These are derived chiefly from pyrogallol and a few probably from phloroglucinol. To this group belong the tannins of oak and chestnut woods, willow bark, sumac, valonia, myrobalans, divi-divi, and algarobilla. The various tannins behave differently in contact with hide and give unlike tannages. This is due in a large measure to other substances associated or combined with the gallotannic acid, among which may be mentioned gallic acid, ellagitannic acid, and ellagic acid, as well as certain acids of unknown formulas, such as catellagic, metallagic, and flavellagic acids, which differ from ellagic acid apparently only in oxygen content.

The tannins of oak wood are methyl derivatives of gallotannic acid mixed with other substances which readily become insoluble in contact with hide fiber. Besides gallotannic acid, the extracts of myrobalans, valonia, divi-divi, and algarobilla contain ellagitannic acid which yields a deposit of ellagic acid either through fermentation or by the action of mineral acids. Extracts of oak wood, divi-divi, and algarobilla contain pyrogallol tannins which resemble both gallotannic and ellagitannic acids.

Gallic acid is found mixed with most pyrogallol tannins, from which it is derived by hydrolysis. Ellagic acid is particularly interesting on account of its importance in the tannage of heavy leather. Perkin has shown that it is a double lactone derived

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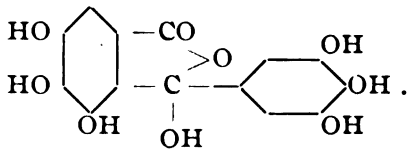
from hexahydroxydiphenyldicarboxylic acid, whose graphic formula, as well as that of ellagitannic acid, is shown in a paper by Meunier.[1]

The formula for gallotannic acid has been the subject of much discussion, since the acid produced synthetically is optically inactive while tannic acid obtained from natural pyrogallol tannins is active under polarized light. Decker gives it the following formula, which contains an asymmetric carbon atom:



Nierenstein considers tannin to be very different from ellagic acid because, when distilled with zinc powder, the former gives diphenylmethane, whereas the latter yields fluorene. By acetylation of tannin, he obtained a pentacetyl compound melting at 203° and a hexacetyl one melting at 116°. He concluded that tannin is a mixture of gallotannic acid, which yields the pentacetyl derivative, and a leuco-derivative, which gives the hexacetyl compound. This is supposed to be the leuco-tannin which makes the natural product optically active.

Catechol Tannins.—These tannins are derived chiefly from catechol and a few probably from phloroglucinol. They are sometimes found mixed with pyrogallol tannins in nature. To this group belong the tannins of oak bark, birch, pine, hemlock, quebracho, mimosa bark, mangrove, gambier, and cutch. When in contact with hide, there is a greater difference in behavior between the various catechol tannins than is the case with the pyrogallol tannins, probably on account of the fact that the former are generally associated with large numbers of foreign substances, notably the catechins and phlobaphenes. The catechins are hydrolytic products of the tannins and only slightly soluble in cold water. Perkin has isolated and studied the catechin from gambier, which has the formula $C_{15}H_{14}O_6.4H_2O$. The phlobaphenes, on the contrary, are condensation products arising from dehydration and oxidation of the catechol tannins. Each tannin possesses a series

[1] *Chimie et Industrie* I, 75 (1918); This JOURNAL XIII, 534 (1918).

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of anhydrides, those more strongly dehydrated being less soluble and more highly colored. Among the catechol tannins may be mentioned quercitannic acid, from oak and mimosa barks, which is capable of fixing 28.4% of bromine, quebrachotannic acid which fixes 43%, and catechutannic acid which fixes 50%. This group of tanning materials contains also a number of complex, colored bodies called flavones.

None of the catechol tannins has yet been isolated in the pure, crystalline state and we do not know their exact structural formulas. Körner has found the molecular weight of the tannin from quebracho to be in excess of 1000, while Paterno holds that the molecular weights of the catechol tannins can vary from 2500 to 3500. The tannins exist in solution only in the colloid state.

Tannins are more readily absorbed by hydrogels from water than from other vehicles. Wislicenus found that freshly prepared alumina absorbed 78% of tannin from aqueous but only 32% from acetic solution. Using quebracho tannins, Körner found an absorption of 99% from water as against only 53% from acetic solution.

Procter, who has studied the phenomenon of tanning quantitatively, has shown that the difference of potential existing between the surface layer of solution immediately surrounding the tannin particles and the bulk of solution decreases as the concentration of electrolyte in the solution increases. When this potential difference becomes sufficiently small, the particles coalesce and and precipitate. When hide is immersed in a tan liquor, the potential difference between the hide jelly and the solution being of sign opposite to that noted above, electrical neutralization results, the tannin becoming fixed by the hide.

Since it has been proved that vegetable tannins are colloids, it is readily conceivable that the question of preparing synthetic tannins does not require that the products be absolutely identical with natural tannins.

Recent Work on the Synthesis and Probable Constitution of Pyrogallol Tannin.—For a long time the formula for digallic acid had been given to the tannin extracted from gall nuts. Walden, in 1897, observed that the natural product differed from digallic acid in several of its physical properties, notably its electrical

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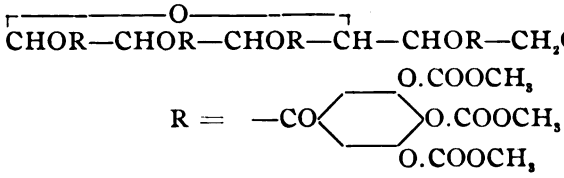
conductivity and its behavior towards light. Furthermore, arsenic acid reacts differently with the two products and the molecular weight of the natural tannin is much the higher. Nierenstein suggested that the natural tannin is a mixture of digallic acid and its optically active reduction product, leuco-tannin, but such a mixture would be more acid and show an apparent molecular weight lower than that of the natural product.

Fischer, in a series of works published between 1906 and 1913 has thrown a good deal of light upon the subject. He purified the tannins from Chinese nutgalls by removing the compounds with free carboxyl groups by means of ethyl acetate, thus obtaining an optically active product. By subjecting the purified tannin to hydrolysis, he obtained one molecule of glucose to 10 molecules of gallic acid. Concluding that tannin is an ester of 5 molecules of digallic acid and one of glucose, he attempted its synthesis. The ordinary mode of procedure was not possible here because the chlorine from phosphorus chloride attacks the hydroxy groups as well as the carboxyl of gallic acid. He therefore began by treating gallic acid with acetyl chloride. The carbomethoxy derivative thus obtained by elimination of HCl is sufficiently stable to permit the reaction of chlorine upon the carboxyl group. It is then easy to replace the hydroxy groups by expelling the carbomethoxy groups by slow hydrolysis. He allowed acid chloride to react with glucose in a solution of chloroform and quinoline, the latter being used to fix the hydrochloric acid formed, and obtained pentatricarbomethoxygalloyl glucose, which is represented by the formula



The compound thus obtained was saponified with a slight excess of alkali dissolved in aqueous solution of acetone and the pentagalloyl glucose isolated. This compound is very similar to tannin, but differs in being optically inactive.

Herzig prepared methylo-tannin and obtained by hydrolysis trimethyl gallic acid and m-p-dimethylgallic acid (asymmetric).

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These facts lead us to suppose that tannin is an ester of glucose with 5 molecules of m-digallic acid. Nevertheless it is possible that some polysaccharides may enter into combination with digallic acid and that the glucose is produced only by hydrolysis of these compounds. The products prepared by the preceding method, using various hydroxy acids and saccharides, possess properties very similar to those of tannins. However, no one has yet been able to prepare these substances at a price anywhere near that of the natural products. Only substitutes have been placed upon the market.

Practical Definition of Synthetic Tannins.—In the industrial world, the word tannage means simply the conversion of hide into leather; that is to say, the sum total of transformations which have for their object rendering the hide imputrescible, resistant to the action of water and dilute chemicals, flexible to a degree depending upon the kind of leather desired, retaining some of the elasticity of the original hide, sufficient resistance to friction, etc. Now the products capable of bringing about these results are very varied in nature. Besides the natural tannins, there are fatty matters, formaldehyde, and numerous mineral products, notably salts of Cr, Al, Fe, Zn, S, SiO_2, etc. All these products are, industrially speaking, tannins. There is therefore nothing extraordinary about seeking among the phenolic compounds for substances capable of producing these same results.

The first researches in this sense were made by Professor Meunier of the University of Lyons. The process of tannage with quinone which he devised was in use in France and Germany before the war. Professor Stiasny of the University of Leeds attempted to synthesize other more complex phenolic bodies and finally obtained some compounds resembling in behavior the vegetable tannins. He made a substitute for tannin which the *Badische Anilin und Soda Fabrik* patented under the name "Neradol D" and which was used in Germany and in England. Quinone and Neradol can be obtained simply and easily as accessory products, and perhaps even as by-products, in the utilization of matter derived from the distillation of coal tar, which the allied countries intend to continue to handle in large quantities after the war.

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Since the tanning industry now suffers and probably will continue to suffer for a long time from the scarcity and high price of vegetable tannins, it is probable that in the future these synthetic products will be used more and more extensively in the manufacture of leather. Moreover their speed of action conforms with the modern processes of rapid tannage.

The object of the present article is to summarize the researches made upon these two substitutes, which are known in commerce as "synthetic tannins", and to give some information as to their use in the tannery.

Quinone: Its Action upon Gelatine and Hide.—In 1908 Meunier andSeyewetz published results of their researches upon the rendering insoluble of gelatine by the action of the following organic compounds: phenol, resorcinol, orcinol, hydroquinone, pyrocatechin, gallotannic acid, pyrogallol, p-aminophenol, chlorophenol, picric acid, monochlorhydroquinone, and the mono- and disulfonic acids of betanaphthol.

The phenols only slightly soluble in water, such as alpha- and betanaphthols, as well as the simple and substituted amines and aminophenols, either when existing in salts or as free bases, do not give precipitates with gelatine solutions. But if conditions are provided favorable to oxidation, both phenols and aminophenols give precipitates which are insoluble in boiling water. This fact led the authors to experiment with oxidation products of the phenols, especially ordinary quinone. They discovered that the gelatine quinone precipitate is the most stable form of insoluble gelatine at present known, for it resists not only the action of boiling water, but even of dilute acids and alkalis. The time required to render gelatine insoluble by means of quinone is less than two hours at 15° C. The quinhydrones react similarly, only more slowly. On the other hand, experiments with formaldehyde gave a product which dissolved completely upon repeated treatment with hot water and which slowly lost formaldehyde when subjected to dry heat. Furthermore it is dissolved in the cold by HCl and dilute alkalis.

The same results were obtained with hide as with gelatine either with phenols and aminophenols in the presence of oxidizing agents or with quinones without oxidation.

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Comparative experiments with other substances capable of reacting with hide substance show that a liquor containing only 1 part of quinone per 100 parts by weight of raw pelt, renders the latter insoluble, transforming it into a leather whose resistance to the action of water, acids, and alkalis is superior to that of any other leather known, chrome leather included, and whose resistance to wear is at least equal to that of the best leather tanned with oak bark.

The analysis of used quinone liquors reveals the presence of hydroquinone which proves that a part of the quinone was used to oxidize the hide substance while the remainder entered into a stable combination with the oxidized hide. Since hydroquinone is readily oxidizable, the yield will be greater if means are provided to reoxidize it. The provision of conditions favorable to oxidation favor this tannage, and the use of catalysts, such as the laccases, artificial peroxidases, and acetates of Mn, Ce, and La, consequently produce a better and more rapid tannage. Meunier has pointed out that oxidases are to be found among the soluble matters given up by the hide during tanning.

Methods of Preparation and Properties of Quinone.—In general quinones can be obtained by oxidation of the corresponding paradiphenol compounds and can also be produced when more than two hydroxy groups are present provided two of these groups are in the para position. They are formed likewise by oxidation of numerous compounds derived from the phenols, such as p-phenolsulfonic acid and p-aminophenol, but the method often employed in laboratories is to oxidize, by means of chromic acid, certain mono-substituted derivatives of benzene, such as aniline.

Among the chief properties of quinone of interest to the tanner are the following. It is soluble in cold water to the extent of only about one-half per cent. but dissolves to a considerably greater extent in warm or acidified solution. In practice it is dissolved in slightly acidified boiling water, but this should be done in a closed tank as the product is volatile and easily carried away in the vapor. Acid solutions are stable for a much longer period than neutral or alkaline ones, and light is harmful in causing oxidation. Quinone solutions should not be brought into contact with metals nor put into wooden vats which have been previously used for

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vegetable tannins, as they will darken in color and lose their property of giving a clear tannage. Quinone is readily kept in the crystalline state either in wooden or tinned containers so long as it is kept dry. It is preferable to prepare solutions only as needed and not to use more quinone than will dissolve.

Application in the Tannery.—Quinone alone, employed to the extent of 1½ parts to 100 of pelt, is capable of completely tanning the stock in a few days. It would therefore seem at first sight that quinone tannage constitutes an ideal process both from the standpoint of speed and of cost. In reality this is not the case and the reason lies in the fact that the leather is sold by weight, a procedure which was established in times past, when hides sold at a price reasonably higher than that of tannin, in order to induce the manufacturer to get enough tannin into his leather to insure complete tannage. Since then the situation has changed and hides have increased in price out of all proportion to that of tannin. The result of this has been, especially in the case of rapid tannages, an increase in proportion of tannin, combined or not, in the leather until now some of the better grades often contain not more than 30% to 35% of hide substance.

It is quite evident that under these conditions tanning with quinone alone cannot compete with tanning with vegetable extracts excepting for light leathers sold by the square foot. Nevertheless on account of its great value as a preliminary tanning agent, it has become an article of considerable importance. Before the appearance of quinone, formaldehyde was employed preliminary to vegetable tanning with the object of isolating and strengthening the hide fibers so as to enable the hide to be put into concentrated liquors without harm. But the formaldehyde does not remain fixed and experience has shown that after storing for some months these leathers undergo change becoming hard. No such difficulty is found with the use of quinone and hides first treated with quinone fix vegetable tannins with remarkable speed without any disadvantage either to the leather or to the modern methods of rapid tannage. Furthermore its use has increased rapidly in the manufacture of all kinds of leather, particularly sole leather.

The *Leather World* (March 10, 1916) devotes considerable space to the use of quinone as a preliminary tanning agent. It

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has been used for sole and strap leathers, where it has been demonstrated that such leathers possess greater resistance to wear than others not so treated. It has also been used for upper leather and has even been employed with chrome leathers.

For box calf it is recommended not to shave the skins too deeply after the beamhouse work, the quinone giving them sufficient suppleness. The operation consists in adding to a soak of 100 kilos. of skin 600 grams of quinone and 300 grams of 80% lactic acid. If the stock has been bated, the acid is unnecessary. For ordinary leathers acetic acid is preferable. The tannage is then carried out with a one-bath chrome liquor, using only 60% of the usual amount of chrome and neutralizing agent, whether borax, sodium bicarbonate or ammonia mixture. Box calf made in this way is better than the ordinary in that it is more permeable to air and give a shoe which is more hygienic and cooler in summer; it is more supple and has a finer grain; and in dyeing, the black is distributed more uniformly, not only over each skin, but over all skins in the same lot, thus increasing the number of first grade skins. When used for colored calf, the proportion of sumac and gambier can be greatly reduced and the grain is never hard or brittle. The same holds true for smooth calf, whether black or colored. Preliminary treatment with quinone of kid skins intended for shoes makes possible the uses of one-bath liquors and the sorting for colors unnecessary.

Neradol-D or Syntan: *Stiasny's Work*.—The object of this work was to prepare, synthetically, substances possessing the essential properties of natural tannins. These products were to have definite compositions which could be modified at will by the introduction of new alkyl groups, making possible the manufacture of a whole series of tannins especially suitable for making all varieties of leather known and even to produce new ones. The use of these tannins, to which the author has given the name "syntans", was to enable one to proceed in the tannery according to fixed rules and without costly groping about. His aim was to eliminate entirely the empirical character of vegetable tanning. He hoped to establish the relation existing between the tanning effect obtained and the chemical constitution of the products employed. The properties of the finished leather would in this case depend directly upon the molecular constitution of the tannin employed. It was of course necessary that the leather should be

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of sufficiently high quality and the new tannins available at a reasonable price.

Stiasny's first publication on this subject appeared in the Journal of the Society of Chemical Industry of Aug. 15, 1913 and may be summarized as follows: Syntans are condensation products which can be obtained by heating phenols with formaldehyde in slightly acid solution and then rendering soluble the resinous products thus formed by the action of sulfuric acid. They can also be prepared by first sulfonating the phenols and then condensing them with formaldehyde under conditions such that only products soluble in water are obtained. According to the author, although the condensation process has not been exactly studied, it seems very likely that a derivative of diphenylmethane is formed which by polymerization leads to the formation of molecules of high molecular weight, which give the product an amorphous character.

These products resemble tanning extracts, but are less colored. Their aqueous solutions possess a semi-colloidal character and diffuse only very slowly through semi-permeable membranes. They precipitate gelatine and give a deep coloration with iron salts. Syntans are precipitated by lead acetate and by aniline hydrochloride, but, most important of all, they tan hides like true tannin.

Neradol-D, the chief syntan now on the market, when used alone gives a pliable and tough leather with very little color, which is characteristic of this tannage. Where other tannins are used, it is employed as a preliminary tanning agent. Like quinone, it protects the grain, which it tans very gently, and the leather does not become brittle after tanning in strong extracts, nor is it sensitive to the subsequent action of light. It accelerates the rate of tannage and does not lesson the yield in weight. It is advantageous both for heavy and light leathers. The author recommends its use for retaining East India kips, and in chrome tanning.

It is curious to see so little detail given, chemical or technical, in a paper treating a subject so scientific as the synthesis of the tannins and delivered before the most important society of chemical industry of the world. Plenty of questions, requests for information, and observations were put before the anthor in the

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discussion which followed, notably by Professors Green and Cobb, and Messrs. Ingle and Hill.

According to Professor Green, the formation of syntan is not so simple as Stiasny suggests. There is no polymerization, but only the formation of highly condensed products. He believes that o-hydroxybenzyl alcohols are formed, followed by condensation. The simple methyl derivative mentioned by Stiasny cannot be formed. The free sulfonic groups would act like tannin and leathers tanned with syntan would be much more sensitive to the action of alkalis than ordinary vegetable leathers.

Later three articles by Stiasny appeared in the Collegium of which two were in reply to German critics. Not one of them was any more explicit on the subject of the constitution and application of syntans than his paper before the Society of Chemical Industry. It is fair to say that in 1912 Stiasny sold his patent to the *Badische* and that they had just put the product on the market under the name of Neradol-D.

Preparation of Syntans.—At the outbreak of the war, the Neradol-D of German manufacture disappeared from the English market, and since it had come to be appreciated as a very useful material, its manufacture was started according to the information contained in the patent specifications, but all sorts of products were obtained. The color varied from reddish brown to black and the consistency from fluid to stiff paste. All contained insoluble matter in appreciable quantities, but seemed, in practice, to behave like Neradol.

The raw materials are: Cresol, $C_6H_4.CH_3.OH$, which is found in coal tar, sulfuric acid, formaldehyde, and caustic soda. The analysis of these materials is easy, with the exception of crude cresol which contains not only the three isomers, but also variable quantities of other phenols, pyradine, etc. An approximate determination of the amount of cresol may be made by forming the barium salt of a measured portion of the sulfonated product and then precipitating the barium with sulfuric acid and weighing the precipitate. Other phenols present will also form barium salts but it is probable in the manufacture that they form other syntans analogous to that of cresol. In any case for products of the same density, the results are comparable.

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The manufacture is divided into three steps, the sulfonation, the condensation, and the neutralization. Wilkinson gives the following description:

(a) *Sulfonation.*—Heat a mixture of equal weights of cresol and sulfuric acid. The operation should be carried to complete sulfonation, otherwise the desired result will not be obtained. On the other hand it should not be more prolonged than necessary lest there be a loss in yield. The time of sulfonation varies from 1½ to 8 hours according to the crude materials employed, the temperature reached, etc. In order to insure complete sulfonation samples may be tested from time to time, but with a little experience one can judge the endpoint simply by the appearance of the product.

(b) *Condensation.*—This operation is carried out in the cold, but is slow and tedious. In determining the endpoint, one has nothing to go by excepting the complete disappearance of phenolic odor which is replaced by formaldehyde vapors.

The sulfonated product is cooled and the formaldehyde poured into it very slowly while agitating the liquor.

The temperature must not be allowed to rise above 35 degrees and may be regulated either by a cooling coil or cold water jacket. The addition of formaldehyde causes a considerable rise of temperature, caused both by the reaction and by the mixing of the formaldehyde solution with the sulfuric acid.

The product should be viscous and of a dark brown color with slightly reddish tint. It is hygroscopic and should be neutralized without much delay.

(c) *Neutralization.*—The product now contains about 25% of acid calculated as sulfuric, which should be partially neutralized so that the remaining acid shall be about normal, or 4.9% calculated as sulfuric. The amount of soda solution necessary must be determined for each lot. The heat of neutralization is very considerable and the liquor must therefore be agitated and kept below 35 degrees by a cooling device. Under these conditions the liquid clears up considerably and loses much of its viscosity. It is possible, when the temperature during neutralization and the concentration and proportion of soda used are allowed to vary, for secondary reactions to set in, causing changes in the nature of

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the compounds obtained to the extent of altering the properties of the final product.

Following this method one obtains compounds analogous to Neradol-D, although differing in the results obtained in tanning. Certain products made in England are superior to Neradol-D, giving leathers which are whiter and more flexible although fully as tough, and are capable of penetrating calfskins in only a few hours.

Application in the Tannery.—The Leather World has published several articles on this subject. T. H. Edwards gives some results obtained with Neradol and indicates the different kinds of tannage to which it is applicable. Its chief value lies in speeding up the tannage and is used in England most commonly to strengthen the tan vats. In a series of 8 vats, the best procedure is to add syntan to the fourth, fifth and sixth vats. In this way, the skins upon entering find a small amount in the first vat and the effect obtained is very gradual. One starts by introducing 10 lbs. of syntan per 100 gallons of liquor into the sixth vat, 7½ into the fifth vat, and 5 into the fourth, and for each lot strengthening with 3 to 6 lbs. more. In this way the tannins are found to penetrate much more rapidly, making fewer vats and less labor necessary, and saving tannin since the stock more nearly exhausts the liquor. Instead of having to run spent liquors over the leaches or to strengthen them, one can safely run them off as they are so nearly exhausted as to contain practically nothing of value. Another advantage lies in the fact that syntan clarifies the liquor and gives a clearer leather, the color of the finished leather depending much upon the color acquired in the vats. It also dissolves much of the suspended matter which is then taken up by the hide, increasing the yield.

As a preliminary tanning agent syntan can be used the same as quinone, but care must be taken to use it only for perfectly delimed stock. For curried leathers, harness, and strap, the operation is best carried out in vats, such as are used for deliming, and takes from 2 to 10 hours. One should start with a liquor of 5 degrees barkometer, containing about 20 lbs. syntan per 100 gallons water. This is very rapidly absorbed and more should be added to maintain this strength, and raise it by the end of 2 or 3 hours to 7 or 8 degrees. Then no more is added; at the end of

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10 or 12 hours the liquor will be nearly exhausted, although it may show a barkometer reading of about 2½ degrees due to matter not absorbable by hide. For sole and heavy curried leathers, it is best to give the treatment in the pits where the leather is suspended for a day or two, although the syntan in this case would not be so economically employed as in the preliminary soak vat.

When used in the pits, treatment is begun with a liquor of 5 to 10 degrees barkometer corresponding to a strength of 20 to 40 lbs. per 100 gallons water. Next day the liquor is strengthened. The skins are left in the pit one day. This is the simplest method, but when dealing with large numbers of skins it is better to operate a series of 3 or 4 pits. The head liquor is made 15 degrees barkometer with 50 to 55 lbs. syntan per 100 gallons water and each time it is used, it drops in the series, becoming the tail liquor after three lots have passed through. A used tail liquor is restrengthened and made the head liquor again. Each lot passes through all four liquors starting with the tail liquor and working up through the head liquor.

Remarks.—When syntans have been employed either in the tan vats or for a preliminary tannage, it is possible to use stronger tan liquors than in the ordinary method of tanning and the tannins penetrate much more rapidly. The tannins appear to contract the grain during the first few days, but the grain again becomes normal. Syntans employed alone give, like quinone, very little weight.

Future of Synthetic Tannins.—With the aid of quinone and syntans, good leathers were obtained during the war by rapid methods, which have now almost entirely replaced the older methods of tanning over which they have many important advantages. Undoubtedly their use will be extended as time goes on. Since 1914 the allied countries have developed to an enormous extent the industries dealing with coal tar and its resulting products, primarily for the manufacture of explosives, but also for the manufacture of dyestuffs and medicines which were formerly supplied by Germany. These industries will probably continue to grow and raw products for the manufacture of synthetic tannins will be plentiful and cheap.

German manufacturers seem to see in the manufacture of these products an opportunity parallel to that which they seized

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in flooding the markets of the world with their dyestuffs and other organic products. It is at least interesting to read the following note published in The Leather Trades Review of January 10, 1919:

"The great German dye works, the Badische Anilin und Soda Fabrik, continue to take out patents for further products based on Stiasny's invention of Neradol. They are evidently convinced that there is a big future for synthetic tanning material, probably as big a gold mine as synthetic indigo has proved, and they appear to be endeavoring to corner this industry by the well known method of taking out numerous patents covering probable alternative methods. There is an addition to German patent No. 262,558, which appears to cover a very wide range of substances capable of converting animal skins into leather."

In order to understand the importance attached to the manufacture of synthetic tannins, it is sufficient to recall that while England imported during 1913 $8,800,000 worth of dyestuffs, she also imported $9,200,000 worth of tanning materials, consisting chiefly of extracts although at this time tanning with oak bark was still the most common method. Now there is no doubt that the development of rapid tanning has caused a diminution in the use of oak bark and that this diminution will continue.

For the past two years the *Badische* has continued to take out patents for sulfonated products intended for tanning. However, it has not been proved that the synthetic tannin industry will develop in this direction. On the contrary various technical journals have called attention to the difficulties occasioned by the use of syntans in making leather. In Germany a move has been made to urge against its use and even to prohibit its use in the manufacture of army leathers.

On the other hand, the latest investigations upon the natural tannins, particularly those carried out in Germany, seem to show that these substances contain quinone-like groups which play the dominant rôle in tanning. According to Moeller (Collegium 1918, p. 71-78) the various other tannages possess points in common with quinone tannage and all tannins have a quinone-like character. The phlobaphenes of quebracho yield anthracene when distilled with powdered zinc, and Nierenstein some ten years ago attributed this reaction to the presence of a hexaoxy-

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anthraquinone. Powarnin found oxyanthraquinone in the tannin of willow bark, which is a pyrogallol tannin. In fact, all phlobaphenes which are formed by dehydration and oxidation of tannins have quinone-like groups in their molecules.

All tanning extracts contain these substances which are kept in solution by the peptizing action of the tannin, and when the latter becomes oxidized, the colloid-chemical character of the solution changes; certain phlobaphenes are precipitated along with some dark colored humins arising from still further dehydration. These are partly absorbed by those phlobaphenes still remaining in solution and are responsible for the darkening of the color of the liquor. On the other hand, the soluble peptizers are converted into colloidal matter very similar to phlobaphenes. As an intermediate product of this oxidation, one always finds benzoquinone whose quinhydrone colors the solution an intense red, which is often attributed to the phlobaphenes themselves. According to Moeller, every oxidation of peptizers in solutions of vegetable tanning materials gives, as intermediate products, certain quinone-like substances, which may even exist in the original plant.

Now substances with quinone-like character possess in a high degree the property of forming peptized colloidal solutions and are in reality the only tanning materials capable of uniting with hide fiber in absolutely stable combination. From the preceding as well as from the modern conception of tanning, it would seem that the process of quinone tannage includes the simplest and probably the most rapid of the phenomena taking place in vegetable tannage.

J. A. W.

ABSTRACTS.

Tanning Materials from Waste Sulphite Liquor. *Bulletin No. 66*, Forestry Branch, Canadian Dept. of the Interior. A review of all available literature pertaining to the subject of the use of sulphite cellulose as a tanning material. A complete bibliography is given.

Effects of Glucose and Salts on the Wearing Quality of Sole Leather. *Technologic Paper No. 138, Bureau of Standards.* Four brands of commercial oak-tanned sole leather were selected for these experiments that differed in the amounts of added glucose and salts they contained, and

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that were made by different methods of tanning. The results of field tests, made by infantry soldiers at Camp Meade, machine wearing tests and chemical analyses of the leathers before and after wear, are given.

The work is summarized as follows:—"It would appear that the four brands of leather tested did not differ greatly in wearing quality. There is no indication that the addition of glucose and salts is either beneficial or detrimental to the durability of the leather. It is shown conclusively the greater part of the added glucose and salts is lost from the leather during wear, while the other water-soluble materials appear to be retained in the leather. It is also shown that two leathers, which were given the same tanning in the layaways and then filled with glucose and tanning material, respectively, by drumming, have the same wearing quality. The method of adding the tanning material, either by drumming or of giving a long-time tanning in the layaways, also appears to have little effect on the wearing quality."

The Nature of the Liming Process. By EDMUND STIASNY, *J. S. L. T. C.* **3**, 129 (1919). A complete translation of the comprehensive researches of Stiasny on the liming process which was published in *Der Gerber*, 1906. Liming liquors are classed as—

(a) Pure hydroxyl-ion liquors (to which belong solutions of caustic soda, lime, baryta and ammonia).

(b) Sharpened limes, (1) lime liquors in which an increase of the hydroxyl-ion concentration has taken place by means of suitable additions.

(2) Lime liquors which have received a proportion of hydro-sulphide-ions by the addition of sulphides (sodium sulphide, calcium sulphide, red arsenic).

The results of the experiments are given as follows:—

1. In pure hydroxyl-ion liquors the action of the liquor depends on the hydroxyl-ion concentration and also on the kind of metal-ion present.
2. The greater the concentration of hydroxyl-ions, the greater the swelling (weight and volume adsorption), the unhairing and loss of hide substance.
3. Taking the bases:—caustic potash, caustic soda, baryta, lime, ammonia; plumping and swelling action decreases in the order given, whilst the unhairing action increases in the order given.
4. Hydroxyl and metal-ions are not taken out of the liquor in equivalent quantities (adsorption of the unaltered base by the hide), but a preferential adsorption of hydroxyl-ions takes place which is proved in a lime and a baryta liquor.
5. Different liquors of equal strength are not absorbed in equal quantities by the hide; the absorption is greatest with lime and baryta liquors and least with ammonia liquors.

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6. The loss of hide substance is dependent on the kind of liquor used as well as the concentration of the liquor. This loss is considerably smaller with lime and baryta liquors than with caustic soda and ammonia liquors, and in consequence the greatest loss of hide substance is in old ammoniacal limes.
7. Gelatine behaves differently from hide in this respect, ammonia liquors for example, show only a small solvent action on gelatine.
8. The sharpening of "limes" with solutions of salts (carbonates, oxalates, sulphates, acetates, etc.) is caused by the formation of insoluble (or only slightly soluble) or undissociated (or only slightly dissociated) lime salts with simultaneous increase in the hydroxyl-ion concentration.
9. Ammonia salts for sharpening lime liquors behave differently from sodium salts as in consequence of the much smaller electrolytic dissociation of ammonia the reaction can proceed much further before the limit of the solubility of the lime is reached.
10. Limes sharpened with ammonia do not show the characteristics of ammonia liquors although ample ammonia be present.
11. In a similar manner the action of ammonia liquors as regards unhairing and swelling is considerably checked by the addition of calcium salts (also barium and zinc salts); this is of importance in the criticism of "old limes."
12. Hydrosulphide-ions alone exert neither unhairing, swelling or plumping action on the hide.
13. The action of liquors sharpened with sulphide of sodium, sulphide of lime or other sulphides depends on the simultaneous presence of hydrosulphide and hydroxyl-ions.
14. For the proper action of the liquor, the proportions of hydrosulphide-ions to hydroxyl-ions is of great importance, the best proportion being 1 : 1; an excess of hydroxyl-ions is only of little influence, an excess of hydrosulphide-ions on the contrary causes an extraordinary reduction in the action.
15. Pure sodium sulphide liquor should not be made with hard water, as the bicarbonates in the latter have an unfavorable action on the proportion of hydrosulphide to hydroxyl-ions.
16. The action of arsenic-limes is, as has already frequently been stated, only to be explained by the calcium hydrosulphide, the practical consequence being to sharpen with calcium sulphide instead of arsenic.
17. The reaction between red arsenic and lime depends on the choice of the proportions of these substances used. With excess of lime calcium hydrosulphide, and calcium sulpharsenite are chiefly formed. With excess of red arsenic no calcium hydro-

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sulphide is formed, but only calcium sulpharsenite or oxysulpharsenite which have no unhairing action.

18. On boiling lime water with red arsenic, metallic arsenic is formed among other products.

19. The calcium sulpharsenite formed by sharpening a lime with red arsenic is changed on heating with water into calcium oxysulpharsenite with evolution of sulphuretted hydrogen.

20. The influence of the oxygen of the air in the formation of the arsenic lime can be proved; but a lime produced in absence of air shows no smaller unhairing power.

21. In regard to the unhairing action of "old limes" the ammonia content does not need to be seriously considered; this was shown by experiment and is also to be concluded from the behavior of ammonia liquors containing lime and lime salts (see 10 and 11). On the other hand the action of an "old lime" was strongly retarded by an addition of chloroform which points to something other than pure chemical action.

Tanning with Silica. ALEXANDER T. HOUGH, *Le Cuir*, VIII, 209, 257, and 314 (1919). The author, who is the inventor of a process for tanning with silica, first conceived the idea in 1911 while perusing the English translation of Poschl's book on colloid chemistry. He read of the classic experiments of Graham, who found that colloidal silicic acid resembles tannin in its property of precipitating gelatine from solution and he marvels that a reaction so definitely established should not have been applied earlier to leather manufacture, having been ignored even by the Germans. Of course the mere fact that a substance precipitates gelatine does not prove that it possesses tanning properties, but it does suggest trying it.

The similarity in action of silica and tannin in precipitating gelatine is emphasized by reference to Wood's paper on the compounds of gelatine and tannin (cf. This JOURNAL III, 183 (1908)). Using an excess of silica, the precipitate was found to contain 178.5 parts of silica per 100 of gelatine; with an excess of gelatine, only 109 parts of silica. These figures illustrate that silica is fixed by gelatine to an extent which is unique for mineral tannage, and this is confirmed in practice; an average leather contains from 17 to 24% of SiO_2. In fact one of the difficulties of the process is to prevent too great an absorption of silica.

At least two others discovered the tanning properties of silica independently. Henri Morin of St. Denis, while seeking a filling agent for use with formaldehyde tannages, tried soaking the leather first in sodium silicate and then in acid. He found that the precipitated silica acted not only as a filler but also as a tanning agent. Experiments carried on without formaldehyde confirmed his findings and he applied for a French patent on Oct. 22, 1914. The author had already applied for a patent in Borneo, where he was staying at the time. A third inventor, Paul Chambard, made application for a patent, but withdrew when he found him-

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self preceded by two others. Chambard, who was assisting Professor Meunier at the Lyons Tanning School, tried using sodium silicate to render chrome salts basic. Up to a certain point he got no precipitate of silica and, after using such a liquor, he found considerable quantities of silica in the leather. This led him to experiment with silica alone and he proved that it actually does possess tanning properties.

According to Morin's patent, the skins, after deliming, are soaked in a bath containing a 2½ to 10% solution of sodium or potassium silicate, using 3 liters per kilogram of hide. The length of treatment depends upon the nature and origin of the skins, but for sheepskins 48 hours should be sufficient. The stock is then soaked in a bath of very dilute acetic acid in order to precipitate and fix the silica. The skins are left in the acid bath for several days and are then thoroughly washed, fat-liquored and dried. This process is supposed to give a white, flexible, washable leather, but in practice does not give a marketable leather and the reason for this is not known, although it may be the silica is precipitated so rapidly that there is not enough made available in the colloid state for satisfactory tanning. Nevertheless the author believes this two-bath process would have real advantages over his own one-bath process, if only it could be made more practicable.

The problem confronting the author was to prepare a very stable solution of silica. A sol of silica purified by dialysis is much too sensitive for practical use as the silica is precipitated by very small amounts of electrolytes, such as would ordinarily be carried by the skins. He finally succeeded by pouring a 30% solution of sodium silicate into 30% HCl until the concentration of free acid was reduced to about decinormal. If the acid is poured into the sodium silicate solution, the silica will be precipitated when the neutral point is approached; the silicate must always be poured into the acid. It is the excess of acid which keeps the silica in solution and so long as the concentration of acid is not allowed to fall below decinormal, the solution is very stable.

In practice the skins are worked through the beamhouse as for vegetable tannage and are delimed, bated, and pickled. They are then put into the silica bath which consists, per 100 parts of hide, of 500 parts of water, 50 of 36° Bé sodium silicate, 25 of salt, and about 17 of hydrochloric acid or enough to make the solution decinormal. The acid-silica mixture is added in 3 portions, one each day for the first 3 days. Samples of the liquor should be titrated from time to time and more acid added, as required, to keep the solution decinormal. Sheepskins are fully tanned in from 3 to 5 days, whereas bull hides require about a month. The resulting leather is perfectly white and should be finished as for chrome. To make white leather, one has only to neutralize and fat-liquor.

Attempts to combine silica and vegetable tannages were not successful, which is perhaps due to the fact that silica and tannin are both negatively charged and probably both tend to combine with the same amino groups of the hide molecule. On the other hand, good leathers can be produced by a combined silica and alum tannage, as the alum is probably fixed by

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the carboxyl groups of the hide molecule. The presence of alum, however, seems to retard the tanning, possibly on account of the condensation of aluminum silicate upon the surface of the skins which hinders the penetration. By giving the skins a light chrome tannage first, the speed of the silica tannage is increased and a more solid leather results. In place of hydrochloric acid, sulphuric may be used, but organic acids, such as acetic, are too little ionized to prevent precipitation of silica.

J. A. W.

Notes Upon Tanning With Iron Salts. VITTORIO CASABURI, *Le Cuir*, VIII, 238 and 261 (1919). (cf. This JOURNAL XIV, 423 (1919)). A detailed description of 9 practical experiments in tanning with a liquor made by mixing solutions of ferrous sulphate, sodium dichromate, and sulphuric acid.

J. A. W.

Science Applied to the Leather Industry. L. EGLÈNE, *Le Cuir*, VIII, 328 (1919). During the war the overwhelming demand for leather forced the question of quality to be subordinated to that of increased production. Such a policy continued in peace times would spell disaster to the industry. A new struggle for commercial supremacy has begun that will require the production of leather of high quality at a low price. Regret is expressed that the commissariat did not know enough to profit by its unique opportunity to prepare for the after-war period, although this is to be expected where chemists and specialists are not represented. But it is the future, not the past, that matters now and the secret of solving present problems lies in the application of science to the industry.

Methods of preserving hides should be investigated by means of our knowledge of antiseptics, bacteriology, and the processes of putrefaction. Both physics and chemistry can be brought into play in determining the best methods of soaking, to prevent loss of hide substance and to deal most effectively with very hard and dry hides. Microbiological and chemical studies should be made of the liming process and of the actions of sodium and arsenic sulphides, both alone and mixed with lime. Much credit is due to Wood for his noteworthy bacteriological studies of bating and to Procter and to Meunier for their works on the theory of tanning. A vast field for scientific investigation is offered in the matter of tanning materials, which are now derived from all three kingdoms of nature.

Although the above survey is brief, it indicates how much the development of the industry is dependent upon the application of science, and the author hopes it may inspire tanners to wish to know more about such matters.

J. A. W.

On the Theory of the Processes in the Oiling of Leather. By W. MOELLER, *Gerber* **45**, 277 (1919). The opinions of the nature of the chemical and physical reactions which take place in the oiling of tanned leather differ widely from one another. Knapp assumed the oiling of leather to

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be a kind of after tannage and considered the fat as a specific tanning material. Hence a barked tanned upper leather that has been oiled would be considered a kind of combination tannage.

The author considers the object and the mode of combination of the fat to be the same in the oiling of tanned leather as in chamois tanning, and therefore the selection of fatty matter to be used should be the same or material that has already been converted. In the oiling of leather two objects are pursued, namely, to increase the imperviousness to water and to augment the softness and flexibility. Both effects are not produced by the same fatty matter and are to be considered separately.

In the oiling of leather by means of train oil, after standing for some time it will be found that decomposition of the oil has taken place and the oil is resolved into solid and liquid constituents. The liquid portion frequently comes out of the leather but such will not occur if oiling is accomplished by means of an emulsion in which solid constituents predominate, as for example degras. The appearance of solid constituents in train oil, which is the same in chamois tanning, is traced to oxidation. That the so-called auto-oxidation is very strongly influenced by bodies of phenolic character has been recognized for a long time. The vegetable tanning materials contain polyvalent phenols and these can easily serve as oxygen agents. Unna[1] has shown that there occurs a kind of reciprocal action when substances containing oleic acid are in contact with phenols, whereby the latter are also oxidized. That a permanent chemical change of the unsaturated fatty acids actually occurs, is confirmed by the formation of oxyacids in the train oil and further by the disappearance of water which existed in the hide or leather, water being essential to this reaction. The author is of the opinion that "evaporation of the water from the interior of the leather is, indeed, very improbable on account of the isolating fatty layer". The presence of water in the oiling of leather with train oil is a prime necessity, not as a means of drawing the oil into the leather as the water evaporates from it, but as a requisite for the chemical reaction whereby the unsaturated portion of the train oil is converted into oxyacids. A dry leather oiled with train oil will absorb it but the chemical changes can only occur very slowly, on account of the lack of water, and such a leather will always remain oily, similar to a piece of paper that has been treated with oil. A wet leather oiled with train oil dries completely without an oily condition.

In the formation of oxyacids the last step in the reaction is an oxygen cleavage of the peroxides, on combining with water, with liberation of oxygen. This free oxygen acts on the easily oxidizable part of the polyvalent phenols of the vegetable tanning material with the formation of bodies that are probably of quinone like character. These compounds are similar to phlobaphenes and their formation are of value for the purpose of increasing the water resistance and diminishing the washing loss of the leather. According to the peptization theory of colloidal tannins[2] advanced

[1] Cignolio als Heilmittel der Psoriasis, Leipzig, p. 30, 1916.

[2] *Collegium*, 1915, 49 and 441. Abstract This JOURNAL, 11, 592 (1916).

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by the author, in upper leather tanned largely with pyrogallol tannins, proportionately large quantities of peptisers of the pyrogallol class are present which on account of auto-oxidation are changed to insoluble peptized substances. This fact has hitherto never been considered and it plainly plays a prominent rôle in the oiling of leather by means of train oil.

The basic principle underlying the action of all mediums for the oiling of leather is traced to colloid-chemical causes, especially to the formation of emulsions. The higher the viscosity of the oiling medium, so much the better is it suited. As an example the author refers to the production of glacé leather, "which is properly not a tannage but merely a lubrication of the hide on a colloid-chemical basis"; that for the production of flexibility the solid constituents, namely the alumina and flour, of the tanning paste are of more importance than the egg oil; and that these constituents play a similar rôle to the particles of graphite in the modern graphite lubricant.

The vegetable tannins have been used since antiquity as peptisers for different kinds of mineral matter. The Egyptians used liquids containing tannin to obtain a uniformly dispersed clay, and Acheson used another kind of tannin solution to obtain the greatest possible dispersion of graphite. For the production of ointments from lanolin and such wax like substances tannin finds extensive use. The physical effect of the peptisers existing in the vegetable tanning materials is also of great influence for the purpose of obtaining the greatest possible dispersion, in the oiling of leather.

On oiling leather by means of such substances that contain no oxidizable unsaturated acids, as for example, dégras, the physical phenomena only occur as the solid constituents already exist.

The author claims that the chemical theory of chamois and oil tannages, which assumes that a part of the oil is combined chemically with the collagen because a certain part of the fat is not removed by any kind of a fat solvent is not necessarily true because it is well known that it is very difficult, if not impossible, to even effect the entire removal of fat from an emulsion containing it. According to the colloid-chemical theories of emulsification the retention of fatty acid or glyceride in hide or leather on a physical basis is intelligible.

G. W. S.

Preparation, Composition and Properties of One-Bath Chrome Liquors. ANON, *Gerber* **45,** 174 and 191 (1919). The simplest way to prepare a one-bath chrome liquor consists of dissolving the chromium compound in water and making the solution basic with soda. If chrome alum or chromic sulphate has been used then the solution will contain sodium sulphate in addition to the basic chromium compound, if chromic chloride has been used then the solution will contain sodium chloride. The degree of basicity plays a material rôle with reference to stability and tanning efficiency and must be suitably regulated. Those chrome liquors are most suitable for tanning, whose basicity lies between the one-third and two-third basic salt and such

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a compound will be obtained if 286 parts of crystal soda is used to 928 parts of chrome alum. Solution should be accomplished with heat for in spite of the opinion often advanced to the contrary there is no difference between the tanning efficiency of violet or green solutions which has been proven in recent experiments.[1]

The preparation of basic chrome liquors can be prepared from the chromium hydroxide residues obtained in preparing basic liquors with soda, by dissolving in the proper amount of acid to give the basicity desired. Such liquors differ from the preceding in that they contain no alkali salts, if the chromium hydroxide residue is washed properly before dissolving.

In the preparation of chrome liquors by reduction with organic matter, an excess is used. These liquors contain besides the basic chrome salts the unchanged part of this matter which, it is assumed, makes the leather softer and milder; and the aldehyde like decomposition products, which is alleged to have a certain effect in view of the tanning properties of formaldehyde. Such solutions will differ from solutions prepared by reduction with inorganic compounds in containing these organic products. Chrome liquors prepared by reduction with sulphurous acid, alkali sulphites with the use of sulphuric and hydrochloric acids will contain the corresponding alkali salts.

In weakly basic liquors the chrome penetrates the hide very quickly but generally it is easily dissolved out again with water. Upon increase in basicity the chrome liquor assumes a more decided colloidal character and within certain limits the more basic a liquor is the longer it will take to penetrate. A too strongly basic liquor will clog the pores of the hide and thereby prevent further penetration.

Frequently in practice neutral salts are added to one-bath chrome liquors on the assumption that it will enhance the absorption of chromium by the hide and that a softer leather will be obtained. Procter and Griffith[2] have found on the contrary that the rapidity of tanning and the amount of chrome absorbed is reduced when using liquors containing common salt. Leather obtained from chrome liquors containing it is less plump than that obtained under the same conditions without salt. The same authors found that the chromium compound contained in the leather is somewhat more basic than the compound contained in the liquor used for tanning. Hence chrome liquors must not only be improved by an addition of fresh liquor but also by the addition of chromium hydroxide or alkali in order to maintain the original basicity. It is not commendable to use a soluble alkali like soda for this purpose as this would lead to an accumulation of alkali salts in the liquor, thereby lowering the tanning efficiency. This can be avoided by using insoluble salts like barium or calcium carbonate.

The stability of chrome liquors, excepting the basicity, depends on the kind of acid and on other salts that are present. Chrome salts of organic

[1] *Ledertech. Rundshau*, No. 29 (1910).

[2] This JOURNAL, 12, 612, (1917).

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acids can be made more strongly basic without separation taking place and on the other hand they give a better tannage at a lower basicity than chrome alum or chloride.

The investigations of Wilson and Kern[3] on the influence of neutral salts on the stability of chrome solutions led to the conclusion that this influence is connected with the degree of hydration of the salts in solution. The more strongly hydrated salt will yield the greatest increase in the stability of the colloidal chromium salt solution. Hence liquors prepared by rendering chromic sulphate basic with soda will be more stable than those prepared in the same way using chromic chloride, since sodium sulphate which is formed in the former case is hydrated in solution to a greater extent than sodium chloride which is formed in the latter case.

Temperature is an important factor on the influence of neutral salts, since with increase in temperature there is a decrease in the degree of hydration of the salts and a corresponding decrease in their effectiveness to stabilize the colloidal solutions.

The addition of neutral salts, according to Procter and Griffith, has the disadvantage that the chrome will be taken up slower and in smaller quantity, however, on the other hand it gives the advantage that more strongly basic liquors can be used, whereby less acid is introduced into the leather to be neutralized.

Next to chrome content, the basicity is looked upon as a criterion for the behavior and the valuation of the tanning effectiveness of chrome liquors and extracts. Thomas and Baldwin[4] suggest that the tanning effectiveness does not depend on the total acid but on the actual acidity or the hydrion concentration. Their researches show that the hydrion concentration changes on dilution and on standing which does not appear in the expression of basicity, also the presence and influence of neutral salts is not included in this expression. Hence two chrome liquors showing the same basicity can have entirely different properties with reference to their stability and tanning power, and the expression of basicity can no longer be considered a criterion.

It appears therefore, that, for an exact valuation of chrome liquors, besides the determination of basicity the determination of the hydrion concentration is necessary and also the determination of organic and inorganic matter present in the liquor.

G. W. S.

[3] *Ibid*, 12, 445, (1917).
[4] *Ibid*, 13, 192, (1917).

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CONTENTS

The Need of a Standard Method for Color Determination. By T. Blackadder and C. L. Garland - - - - - - 181

Emulsions—Theory and Practice. By Arthur W. Thomas - 186

The Shake Method and Filter Method in the Analysis of Tanning Materials with Hide Powder. By G. Baldracco and S. Camilla - 201

Abstracts - - - - - - - - 212

Patents - - - - - - - - 217

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W. K. ALSOP . . . . . Editor and Manager
G. W. SCHULTZ . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

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THE NEED OF A STANDARD METHOD FOR COLOR DETERMINATION.

By T. Blackadder and C. E. Garland.

Received Jan. 16, 1920.

The question of color measurement of tanning solutions has always been a moot question. The literature in the past contains many accounts of work done with skivers and various substitutes for skivers and various color measurements, but even today the question is as unsettled as it was ten years ago. It appears that

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skivers will always be of supreme necessity, but some determination which can be recorded in black and white on paper is equally necessary. The importance of the question has again been raised by the development of our European trade in tanning materials. The European market depends in part upon measurements of color with the Lovibond machine for a valuation of tanning materials. The difficulty at once arises that this method even in experienced hands is influenced by some undetermined factors which make the concordance of readings difficult if not impossible when these readings are made, either by different operators working as nearly as possible under the same conditions, or even by the same operator working as nearly as possible under the same conditions but in different localities, or with different machines. This point has been recognized for a long time and many improvements have been suggested and tried out in order to effect concordancy of readings made on the Lovibond machine, but, judging from the fact that this machine is still used in practically the original manner, it would seem that these attempts have been attended with only indifferent success. Notable among these attempts is the suggestion by Procter of using the Schmidt & Haensch Machine, which machine uses a field divided by a hair line instead of two windows as in the Lovibond machine, thus rendering a closer matching possible. At the same time, by holding down the total number of color units to ten he effects a further concordance, but apparently with a loss in accuracy. Another improvement was suggested by Kerr where artificial lighting is made use of in order to avoid the differences due to a northern daylight in various localities. Kerr also suggested the use of dye solutions instead of the regular Lovibond glasses, recognizing one fault inherent to the Lovibond glasses, namely, that they are not always alike. That is, a five units red glass used in one laboratory may not be exactly the same as a five units red glass which is being used in another laboratory.

In looking over the field of past endeavor it appears that very little has been mentioned of the theory underlying the measurement of colors, most of the development having been carried out along the line of getting something to work, out of the material already at hand. The writers, after several years ex-

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perience in the use of the Lovibond and Schmidt & Haensch machines, and after trying all the published modifications, and several others, perhaps better left unmentioned, think that possibly the subject could be more successfully attacked from another angle.

When we see color in light after it has passed through a solution we know that the solution has absorbed certain colors out of the white light entering it and allowed the remainder of the colors to pass through. The eye receives all the various colors which pass through and blends them into the color which we see. We realize, of course that there are an infinite number of colors blended together in the white light, there being a different color for each different wave length. In order to get a definite finding on what color the solution is, we are faced with the problem of determining which colors are let through or which colors are absorbed. Now, the Lovibond machine attempts to do this by matching the apparent color of the solution against the apparent color built up by various combinations of three arbitrary colored glasses. Leaving aside for the moment the fact that these glasses are not exactly standardized, we will confine our observations to the fact that these glasses are of no definite color. By this we mean that a red Lovibond glass looks red but does not pass red light only, in fact when examined in the Spectroscope it appears that it absorbs one broad band in the green and lets through red light, yellow light, some green light, and an abundance of blue light. Correspondingly, the yellow glass lets through red light, yellow light, green light and a considerable proportion of blue light, absorbing only some blue and violet light. The blue glass, correspondingly, lets through practically all colors absorbing only some of the yellow light. These glasses therefore are by no means pure colors and as the different colored glasses let through lights of the same color, it is only too easy to have the same effect on the eye produced by various combinations of the glasses. Those of us who have worked with the Lovibond machine will probably have noted that varying our blue will cause a variation in our ratio of red and yellow glasses. In fact it is often possible to make color matches in the Lovibond machine with or without blue in the combination. In view of the fact that the blue is very often

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the determining factor in the valuation of an extract for the European market, this point would seem to render a correct valuation by means of this machine impossible. In short, any method which is used for measuring the various colors let through by the tanning solution must depend upon using pure colors as its standard. By pure colors we mean that the light let through by the standard must be all in one definite band of the spectrum and not a conglomeration of different bands which when seen by the eye are combined to make an apparently pure color; also the standard colors employed must not overlap, that is, no two of the color standards must contain the same spectroscopic band or we will be faced with the possibility of different combinations of our standard letting through the same total color; and thirdly, it is questionable if it is possible to match a colored solution against a combination of pure color standards with the aid of the eye alone, because, on account of the combining properties of the eye, it is possible that when we see the same color in the solution and in the standard, we really have different components. The question therefore appears to be, can we observe each color separately and determine whether or not each particular color is absorbed or let through by the tanning solution, and to what extent. At first sight it would seem that this would call for an indefinitely large number of pure color standards but for practical purposes it appears feasible to divide the spectrum into three portions, say, the lower third, the middle and the upper third. This is really a division of white light into the three primary colors, red, green, and blue-violet. If now we have a means for throwing each of these three parts of the spectrum through our solution independently, and observing what percentage of light in each is passed through we ought to have a means of evaluating the color of the solution.

The writers claim no especial originality in these remarks. As a matter of fact, the Hess Ives Tint Photometer, which is already on the market embodies the principles outlined above and offers the means for effecting measurements of color in the manner suggested. The following description of the apparatus is probably fitting at this point as it is not well known in the trade.

In this Photometer white light is passed through two windows,

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in front of one of which the colored solution is placed and in front of the other, a movable shutter is placed. The light after entering the windows passes through a suitable prism in order to give a field divided by a hair line so that very minute differences in the two sides of the field can be readily observed. In order to observe only one color at a time a color screen is used directly in front of the observer's eye. This screen is a pure color screen and permits only one broad band of the spectrum to reach the eye at one time. A red screen is used for the lower part of the spectrum, a green screen for the middle part, and a blue-violet screen for the upper part. Beginning with the red screen in position we can determine the amount of red light let through by the colored solution by partly closing the shutter in front of the other window. This shutter, having a scale divided into one hundred divisions, the readings are directly in percentages of the total light in the red band entering the solution. With the shutter wide open the appearance to the eye is of a red field one half of which is brighter than the other, the bright side being of course, the side where the light is coming through the open shutter, the other side being darker because the solution does not pass all the red light entering it. If we partly close the shutter the bright half of the field grows darker, approximating to the duller half. By closing the shutter the proper amount, the fields have a uniform appearance and then we know that an equal amount of red light is reaching the eye through each of the windows. Supposing that the shutter is exactly one half open at this point, then we know that the colored solution is passing half of the red light that is entering it. So far as the green and blue-violet lights go we are not interested because they are entirely stopped by the red screen and do not effect the eye.

We can then perform the same operation with the green, and finally with the blue-violet screen in position and in this manner obtain three different measurements, the first representing the amount of red light, the second representing the amount of green light and the third representing the amount of blue-violet light let through by the colored solution.

From the above description it will be seen that a machine of this type measures color on an entirely different basis from

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machines using combinations of colored glasses. The writers have done some work with the apparatus in question with a view to finding out if it were practical for the purpose under discussion. Perhaps the two main points which must be satisfied are firstly, concordance between different operators and secondly, concordance with different illuminations. On both points the machine appears very promising. On account of the indications shown by our work up to this stage it seems advisable to acquaint our fellow members with a fundamentally different system, which we believe, may effect a concordance in color measurement and give a true measure of color. We intend to pursue this work further and any criticism or suggestions would be appreciated.

EMULSIONS—THEORY AND PRACTICE.

By Arthur W. Thomas.

Received Jan. 29, 1920.

Fat-liquors are emulsions. While the practical process of fat-liquoring is carried out successfully by means of special treatment for each particular kind of leather; special treatments found by the "cut and try" method, the fundamental principles involved are obscure. It is generally admitted that an elucidation of the chemistry and physics of fat-liquoring will be of great benefit to the tanning industry.

A theory attempting to explain fat-liquoring of chrome leather has been given by J. A. Wilson, [1] and it is the first on record,—

Wet chrome leather containing a small amount of hydrochloric acid ionizes as follows:—

$$(Cl.NH_3.R.COO)_3Cr \rightleftharpoons (NH_3.R.COO)_3Cr^{+++} + 3Cl^-.$$

If this leather be treated with an emulsion where the emulsifying agent is sodium stearate the particles of emulsified oil are negatively charged due to absorption of stearate ions and combination will take place between the positively charged leather and negatively charged oil particles, thus:

$$(NH_3.R.COO)_3Cr^{+++} + 3(\text{oil-stearate})^- \rightleftharpoons (\text{oil-stearate} - NH_3.R.COO)_3Cr.$$

[1] This JOURNAL, 12, 108.

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It is obvious that in order that the above reaction take place, the leather must be in a slightly acid condition in order to ionize and assume a positive charge which is essential for combination with the oil particles. Excess acidity must be avoided or the emulsion will be quickly broken resulting in various troubles such as spewing, etc.

Before a working hypothesis can be developed which will explain all cases of fat-liquoring, it is obvious that the theory of emulsions must be developed. With this object in view, the following discussion has been prepared. Fat-liquors, whether simple soaps or sulphonated oils are the emulsifying agents, are oil particles dispersed in water. A discussion of emulsions is not complete, however, unless the water-dispersed-in-oil-type be included. The paragraphs which follow cover both classes.

An emulsion is a heterogeneous system consisting of one liquid dispersed as tiny droplets in another liquid.

It has been definitely established that three phases are essential for the formation of a stable emulsion: (1) Liquid A, (2) Liquid B and (3) an emulsifying agent, and the two liquids must be immiscible, or nearly so, in one another. The common types of emulsion considered are those wherein water constitutes one of the liquid phases, and two main types are recognized: (1) a liquid (oil, for instance) is dispersed in water, (2) water is dispersed in oil. The factor which controls the type of emulsion, i.e., as to whether water or oil is the external phase, is the nature of the emulsifying agent.

In general, if the emulsifying agent is more easily wetted by water than by oil, water will be the external phase and oil the dispersed phase; while if the emulsifier is more easily wetted by oil than by water, the reverse will be true. Or, as Bancroft puts it (J. Phys. Chem. **17**, 501 (1913): If the surface tension between liquid A and the emulsifying agent is lower than the surface tension between liquid B and the emulsifying agent, liquid A will be the dispersing and liquid B the dispersed phase. Since the emulsifying agent is almost always recognized as a colloidal substance, it is fairly safe to say that a hydrophile colloid as emulsifying agent will emulsify oil in water and a hydrophobe colloid will emulsify water in oil. This latter state-

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ment is subject to modification, however, which will be considered later.

The method of detecting which type of emulsion one has is very simple. Consider any emulsion of oil with water. An emulsion of oil-in-water (i.e., oil dispersed phase and water external phase) will disperse in water when added to an excess of water, but will not mix with an excess of oil. The converse is true for a water-in-oil emulsion. In short, an emulsion will freely mix or dilute with more of its external phase but not with more of its internal phase.

Robertson (Koll. Zts., **7**, 7 (1910)) suggested a method of staining with Soudan III (a fat-soluble dye). He stated that if Soudan III is sprinkled upon the surface of an oil-in-water emulsion the red color will be confined to the oil droplets and a mass of discontinuous red specks will result, whereas when sprinkled on the surface of a water-in-oil system it will become uniformly red all over. This test has lately been severely criticized, and it has been shown that it led Robertson into misinterpretation of his olive oil-water-NaOH-emulsions. He claimed to show critical concentrations leading to emulsions of water-in-oil. This has since been shown to be highly improbable. The dilution test above mentioned is reliable.

OIL-IN-WATER EMULSIONS.—There are three great classes of this type of emulsion:

(1) The emulsifying agent is an electrical charge on the oil particles, probably due to selective adsorption of OH^- ions of water by the oil particles.

(2) The emulsifying agent is a water-soluble colloid.

(3) The emulsifying agent is an insoluble, or very slightly soluble colloid.

The agent may also be a combination of two or three of the above.

Class (1) emulsions are the simplest of the three and will be discussed first. They may be prepared in any of three ways, (Lewis-Koll. Zts., **4**, 211 (1909)):

(a) A small amount of mineral oil (2 cc.) is shaken with a larger volume of water (100 cc.) for 48 hours.

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(b) Drop of mineral oil is boiled with excess water under a reflux condenser for 30 hours.

(c) Small amount of mineral oil dissolved in alcohol is poured into water resulting in emulsion immediately.

Lewis found the size of the particles in these emulsions to be alike no matter how made and of the order of 0.4 micron. They are negatively charged, the potential difference of the double layer (Helmholtz effect) being –0.05 volt. His measurement of the size of the charge on the droplets, by electrophoresis method, indicated 4.4×10^{-7} electrostatic units. These emulsions owe their stability to the electrical charge and Brownian movement. They are identical with those observed in the condensate from reciprocating, or other steam engines.

The origin of this electrical charge is obscure. Ellis (Z. Physik. Chem., **78**, 321, (1912)) ascribed it to difference in dielectric constants according to the rule of Coehn that a substance of high dielectric constant is positive to one of a lower dielectric constant when one is dispersed in another. This, to be sure, does not explain. Ellis prepared mineral oil emulsions by the shaking method and obtained a concentration of one part oil in 10,000 parts of water, the size of the particles being 1 to 2 microns in diameter, and the specific conductivity of the emulsion was 18×10^{-6} mhos. He found the potential of the double layer to be —0.05 volt, as Lewis did; but his measurement of electrical charge showed on the average 2.12×10^{-6} electrostatic units for the 1 micron particles. He also noted that they were most stable in the presence of 0.001 normal NaOH and ascribed the stability of this type emulsion entirely to the electrical charge, stating that surface tension had nothing whatever to do with it.

Hatschek (Koll. Zts., **9**, 159 (1911)) suggested that the stability of such mineral oil emulsions might be due to the fact that the specific gravities of the phases were close to each other but Groschuff (Koll. Zts., **9**, 257 (1911)) contested this view.

Powis (Z. Physik. Chem., **89**, 91 (1914)) prepared this type of emulsion by the shaking method and determined the double layer potential to be —0.046 volts which checks fairly well with Lewis and Ellis. He studied the effect of addition of electrolytes to the emulsion and noted that anions have the power to increase this negative potential, while cations decrease it. Very small

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amounts of KCl and $K_4Fe(CN)_6$ (up to 0.001 molar) increase it, while larger amounts decrease it. Salts with polyvalent cations always decrease it due to the predominating positive charge of the cations over the anions. He noted later (Z. Physik. Chem., **89**, 179 (1914)) that while an immediate sharp change in the contact potential is noted upon addition of salt, there always ensues a secondary slower change. In the case of a salt like $BaCl_2$, the change is continuous in the same sense, whereas, in cases like $AlCl_3$, it reverts back a little due to loss of Al^{+++} on account of hydrolysis. Powis' studies on coagulation of these emulsions by means of electrolytes will be discussed later.

OIL-IN-WATER EMULSIONS OF CLASS 2.—Where emulsifying agent is a water-soluble colloid.

Good emulsifiers of this class reported are: sodium and potassium soaps, egg albumin, egg yolk, glue and other water-soluble proteins, gums arabic (acacia), tragacanth, Irish moss, milk, starch, saponin and quillaia bark extract.

Previous to 1899, NaOH was classified as an excellent emulsifying agent for fatty oils in water, but Donnan's investigation (Z. Physik. Chem., **31**, 42 (1899)) showed that its emulsifying powers were really due to the soap formed by interaction with the small amount of free fatty acid that is always present in fatty oils. He proved this by means of the drop number method, and stated that those fatty acid salts which greatly lower the surface tension are good emulsifiers, and that since they lower the surface tension they must concentrate in the surface layers about the droplets of oil. Since the soap layer is still more concentrated at the points of contacts, when bubbles happen to come together, capillary forces tend to separate them.

In a later work, Donnan and Potts (Koll. Zts., **7**, 208, (1910)) measured the drop numbers of aqueous solutions of the sodium salts of the fatty acids. They noted that all lowered surface tension, increasing with the molecular weight, but that it is strongly evident first with sodium caprylate. Emulsifying powers are not evident with this salt, but commence with sodium laurate. The emulsifying power increases with increase in concentration in soap to $\frac{N}{300}$ soap solution, above which it decreases due to coagulating effect of Na^+ ions.

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They objected to Pickering's theory (see later) and stated that stability of emulsions is due partly to the electrical charge and partly to presence of surface tension lowering substances which, according to the theory of Willard Gibbs, must concentrate in the surface layer.

A classic study of emulsions was published by Pickering in 1907 (J. Chem. Soc., **91**, 2001). He pursued his investigations in order to make a suitable germicidal spray for agricultural purposes. In all his experiments he emulsified a paraffin oil in water, by pumping it back and forth through a rose nozzle garden syringe. He found potash soaps to be better than sodium soaps as emulsifiers and noted that a certain critical concentration of soap was required for each proportion of oil and water, e.g., to emulsify 75 volumes oil with 25 volumes of water, the latter must contain 0.7 — 1.8% potash soap. For 40 volumes oil to 60 H_2O, — 0.3% —25% soap can be used.

He noted that soaps vary greatly in emulsifying power, some brands being useless and, in fact, two batches of the same brand may show wide differences in emulsifying power. He noted also that while rise in temperature facilitates emulsification, it has no influence on the composition.

Pickering's 70% — 80% oil emulsions were viscid like thick cream, even when benzine was used. Size of particles about 0.1 micron. With 1 cc. of 1% potash soap solution he succeeded in emulsifying 99 cc. of paraffin oil in it, by successive additions of small portions. This famous emulsion was pure white and as stiff as a blanc mange. It could be diluted with water but not with oil, hence, proof that it was of the oil-dispersed-in-water type.

He noted that his strong emulsions were poor conductors of heat. In heating a beaker of such an emulsion it is possible to heat up to boiling at 160° —170° C. for several minutes, while the center is less than 100° C.

When kept in closed vessels they were permanent for months, but cracked soon after exposure to *dry* air.

Strange to say, his emulsions generally separated, no matter what the starting composition, to form a permanent 65-82 volume per cent. emulsion of oil in H_2O.

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Five emulsions of "Solar Distillate" (a paraffin oil distilling between 240° and 350° C.) were prepared as follows:

(1) 67% vol. oil	in 1% soap solution.
(2) 50% vol. oil	
(3) 33% vol. oil	
(4) 50% vol. oil	in 5% soap solution.
(5) 50% vol. oil	in 0.2% soap solution.

After twelve weeks standing they had all separated into emulsions containing from 72% to 82% oil (as emulsion) in upper layer and water below. One-quarter of the column of emulsion from the top in each case deviated but slightly from 84.5% oil. Analysis shows a steadily decreasing oil content in the emulsions from the top downwards. The effect of decreasing the soap percentage is to increase the size of the globules finally to a point where permanence is no longer possible. Pickering reported some novel effects with solid emulsifying agents which will be discussed under that heading later. Of the water-soluble emulsifiers he comments as follows. Soap is best. Dissolved starch, milk and flour are good although the latter gives a flocculent rather than a creamy emulsion and milk forms solid clots. Glue is good. Egg-albumin is good but gives rather frothy effects owing to inclosing air bubbles. Saponin and quillaia bark are good if proportion of oil is small.

In 1912, Newman (J. Phys. Chem., **18**, 34) reported results of attempts to emulsify water and benzine using oleates. He found that when benzine and water are emulsified by sodium oleate, water is always the external phase and that it is possible to make homogeneous emulsions up to 0.5% benzine, and from 80% to 90% benzine. Failure to make the intermediate emulsions, is ascribed to his method of shaking. He made a stiff jelly with 99 cc. benzine and 1 cc. water using 0.05 gm. sodium oleate. This emulsion was stable for more than six weeks. With his shaking machine it was possible to get concentrated emulsions only by gradual addition of the liquid which is to be the internal phase.

Briggs (J. Phys. Chem., **19**, 210 (1915)) measured the amount of sodium oleate adsorbed by benzine emulsions in water and found that the amount of soap adsorbed increases with the degree of dispersion of the benzine particles. He constructed an in-

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geneous laboratory type of homogenizer for the preparation of emulsions. This homogenizer is shown in Fig. 1.

In a subsequent paper (J. Phys. Chem., **19**, 479 (1915)), Briggs and Schmidt find that the drop number test cannot be used to judge the emulsifying power of an emulsification agent for benzine in water. While 1% solutions of gum arabic and gelatin gave lower drop numbers than water when benzine was run into these solutions from a drop pippette, still the gum and gelatin will emulsify benzine in water, due no doubt, to the elastic semi-solid films which they form around the benzine droplets. They are not so good as soaps, however. The optimum amount of soap to form a good emulsion was found to be 0.01% of the total volume.

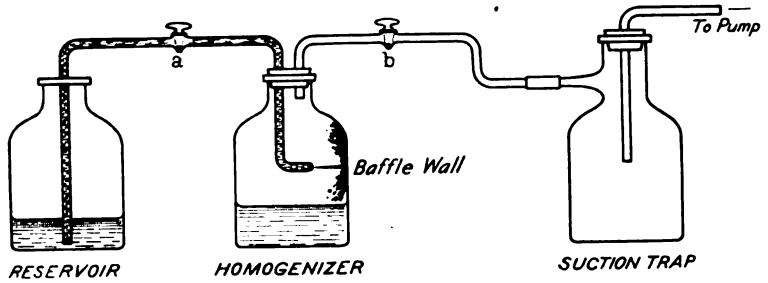

Fig. 1.—The reservoir contains the emulsion mixture which has been shaken up. To commence homogenization, stopcock "a" is closed, "b" is opened and the pump started. As soon as the homogenizer vessel is evacuated, stopcock "b" is closed and stopcock "a" is opened resulting in the stream of mixture impinging against the wall of the bottle as pictured in the figure. These operations are repeated until the desired result is attained.

Fischer's theory of emulsions (Science, **43**, 468 (1916)) is that a hydration compound is essential, i.e., the oil globules must be covered with films of a hydrated colloid. He evidently is not familiar with the lubricating oil emulsions of Lewis, Ellis, Powis and Hatschek nor with the solid emulsifying agents of Pickering.

Roon and Oesper (J. Ind. Eng. Chem., **9**, 156 (1917)) and Crockett and Oesper (ibid. **9**, 966) studied emulsions used in pharmaceutical practice. By the trituration-in-a-mortar method they learned that it is best to add the proper amount of water to

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the internal phase and the emulsifier and then triturate, and that it is best to form an emulsification nucleus in this manner which can be modified afterwards. The proportions giving the best results are,—4 parts oil, 2 of gum arabic and 3 of water. This nucleus is miscible in all proportions with water. Nuclei of one composition act as stabilizers for incomplete emulsions of other compositions, and nuclei of one composition act as emulsifiers for other internal phases. They found Irish moss and gum tragacanth cannot be used with turpentine and forms unmanageable masses with fatty oils. They say "traces" of soap crack Irish moss emulsions while they aid gum arabic emulsions. They are inclined to accept Fischer's hydration theory.

Davey (Physical Review **11**, 138 (1918)), in searching for a substitute for organic solvents in japan varnish found that he could emulsify linseed oil with water by addition of ammonium hydroxide and slowly stirring in a closed heated receptacle. He made the interesting discovery that such emulsions scum when exposed to air containing carbon dioxide at a temperature of 17°C., or higher, but not when exposed at 16°C., or lower, or to air free from carbon dioxide at any temperature. The particles of dispersed phase were negatively charged. This emulsion proved to be a good paint.

OIL IN WATER EMULSIONS OF CLASS 3. EMULSIFYING AGENT IS AN INSOLUBLE OR ONLY SLIGHTLY SOLUBLE POWDER.

Tfol (Pharm. J. (4) **6**, 1228 (1898)), reported that Arabs in Northern Africa used an argillaceous earth as a substitute for soap in washing linen. He found that this earth readily emulsified oils in water.

Pickering (l.c.) was probably the first to study the efficacy of certain solids as emulsification agents. He found that basic copper sulphate (made by adding to 7 parts $CuSO_4.5H_2O$ in solution in water, 1 part of CaO). At least one part of $CuSO_4.5H_2O$ converted to the basic salt is needed to emulsify 120 parts of paraffin oil. Immediate and stable emulsification results and the product is very efficient as a germicidal spray in agriculture. These emulsions resembled his potash soap emulsions in all properties, except that the stable layer contained about 40% oil. The ratio of CuO to emulsified oil was fairly

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constant,—about 0.92 parts of CuO to 100 parts of oil. His experiments with other solid substances yielded results as tabulated below.

Substances which emulsify.—Basic ferrous sulphate, basic copper sulphate and basic nickel sulphase are the best. Ferrous and ferric hydroxides are good. Basic zinc and basic aluminum sulphates give good emulsions temporarily. The precipitate formed by adding sodium carbonate to copper sulphate is good. Calcium carbonate and arsenate are good when freshly precipitated but they soon become crystalline and de-emulsification follows. Lead arsenate and some unheated fine clays are good. Hydrosulphide of iron is good for small amounts of oil and zinc oxychloride is fair.

Substances which produce quasi-emulsions.—Lime, silica, alumina and plaster of Paris which have been dried, and also the following when freshly precipitated act,—basic cadmium sulphate, magnesium hydroxide, copper hydroxide, basic zinc and aluminum sulphates, tin oxychloride, lead arsenate paste, copper sulphide, iron sulphide.

Little or no emulsifying power.—Precipitated lead chloride, lead sulphate, barium sulphate, silica hydrosol, sulphur, flowers of sulphur, Paris green, alcoholic solution of resin precipitated by water, ferrous ferricyanide, ferric ferrocyanide and purple of Cassius. In these cases the oil seems to wet the precipitates more than water does.

Later Pickering stated (Koll. Zts., **7**, 11 (1910)), that while high viscosity and low surface tension of a liquid facilitates the emulsification of an oil in it, yet it is possible to make an emulsion in a liquid which does not possess these properties The most important condition is the presence of small particles insoluble in the dispersion medium which coat over the oil particles and prevent them form coalescing. In order that such particles have the power to form emulsions they must show only a slight tendency to unite with one another, must be readily wetted by water and must not be crystalline. He also made the novel discovery that potassium cupric tartrate will emulsify a mixture of alcohol and water. If this salt be added to an aqueous solution of alcohol, it will cause the water and alcohol to separate into two layers. Agitation results in emulsification.

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Hofmann (Z. Biologie **63**, 395 (1914)), used silver dichromate to emulsify chloroform in water.

In 1915, Briggs and Schmidt (l.c.) found that colloidal ferric hydroxide (formed by hydrolysis of ferric acetate solution), was a fairly good emulsifier for benzine in water.

Emulsions of Water in Oil.—Calcium and aluminum soaps are used in lubricating greases. Holde published a discussion of these greases in 1908 (Koll. Zts., **3**, 270). They are solutions of lime soaps (15-23%) in heavy mineral oil with 1 to 4% water emulsified in them. Some American lubricating greases, especially for automobile, consist of aluminum soaps dissolved in mineral oils and quite large amounts of water emulsified in them by the aid of rosin.

Bancroft (J. Phys. Chem., **17**, 501 (1913)) states that lanoline is an emulsion of water (22-25%) in wool wax and that it is possible to emulsify as much as 80% water in wool wax. The writer believes that this may be due to the cholesterol which wool wax contains. These emulsions are stable for years.

Newman (l.c.) found that while sodium oleate emulsifies benzine in water, magnesium oleate emulsifies water in benzine. He stated that it is never possible to emulsify water in an oil by means of sodium soaps, contrary to Robertson's findings. By using proper procedure he succeeded in emulsifying 96% water in benzine. The stability is increased by the addition of a little sodium oleate. He stated that in mixed paints, water is dispersed in the oil and that this is due to the presence of rosin as an emulsifying agent, and not to the pigments. In conclusion he presented his theory that whether one liquid is emulsified in another or not depends upon the emulsifying agent. A hydrophile colloid will tend to make water the external phase, while a hydrophobe colloid will tend to make water the internal phase and the colloid must be able to form a suitable coherent film around the globules to be an emulsifying agent.

Briggs and Schmidt (l.c.) found that for emulsification of water in benzine;—

Magnesium oleate is fair (forms quasi-emulsions, finer than aluminum palmitate)

Magnesium resinate, copper resinate and leadoleate are unsatisfactory.

Aluminum palmitate forms quasi-emulsions.

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Clowes (J. Phys. Chem., **20**, 407 (1916)), has performed some striking experiments with soap emulsions of olive oil and water. By addition of calcium chloride to an emulsion of oil in water (with sodium oleate as emulsifying agent), when the calcium concentration exceeds the chemical equivalence to sodium, the emulsion passes through a critical point and changes to water dispersed in oil. He found that Na, K, and Li soaps emulsify oil in water while Mg, Sr, Ba, Fe and Al soaps emulsify water in oil. The first series of soaps are soluble in water and not in oil while the second series are soluble in oil but not in water. The alkali soaps are wetted more by water than by oil and since it is thought that the surface tension is lower on the water side than on the oil side of the globules, the film will bend convex to the water and concave to the oil, enveloping the oil articles, because the area of the inner surface of a sphere is less than that of the outer surface. Similar reasoning holds for the dispersion of water in oil by the other soaps mentioned.

Clowes illustrates this phenomenon by the following diagram.

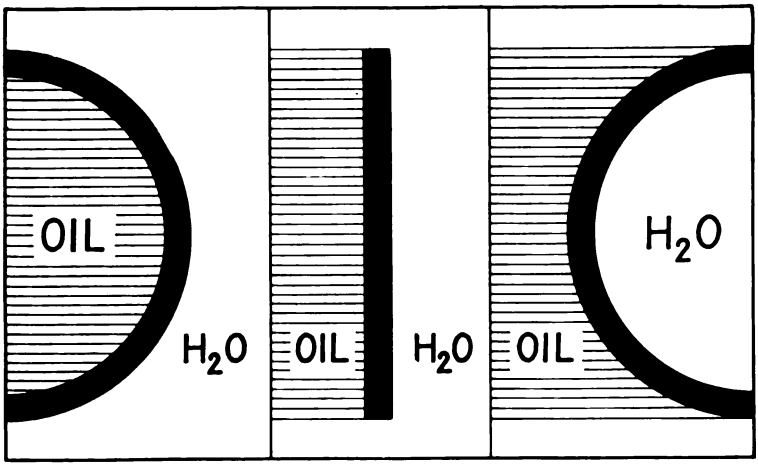

Fig. 2.

	1	2	3
Emulsifying agent or film	Sodium oleate alone or sod. oleate in excess of calcium oleate equiv.	Equiv. chem. proportion sod. oleate and calcium oleate.	Calcium oleate alone or calcium oleate in excess of sodium oleate equiv.
Emulsion formed	Oil in water.	Critical point.	Water in oil.

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In 1918, Schlaepfer (J. Chem. Soc., **113**, 522), reported his experiments with carefully purified carbon black (gas black, soot) as emulsifying agent. This substance must be wetted more by oils than by water because in all cases he obtained dispersions of water in the oil and never oil in water. As dispersion media he used kerosene, turpentine, benzine and toluene. With 60 cc. kerosene, 240 cc. water and 1.5 gm. soot, he obtained an almost solid emulsion.

Moore (J. Am. Chem. Soc., **41**, 940 (1919)), checked Schlaepfer's results. He was able to emulsify water and ammonium chloride solutions in kerosene with lamp black. Highly calcined lamp black and petroleum coke would not function as emulsifying agents. As the concentration of the ammonium chloride solutions was increased, the drops grew larger due to higher surface tensions of the solutions.

Breaking of Emulsions.

In general, de-emulsification can be accomplished by

(1) Addition of excess of dispersed phase.
(2) Addition of a liquid in which the two liquid phases are soluble.
(3) Destruction of the emulsifying agent.
(4) Filtration.
(5) Heating.
(6) Freezing.
(7) Electrolyzing.
(8) Salting out, *i. e.*, lowering potential difference of double layer.

The problem of breaking mineral oil emulsions in steam engine condensates has interested engineers for a long time.

Hatschek (J. S. C. I., **29**, 125 (1910)) offered a solution of the difficulty in a filtration method. He found that such emulsions when filtered through amorphous magnesium carbonate or calcium carbonate (causticizing mud) came through free from oil. On a 4½ square foot filtering surface covered ⅛ inch thick with amorphous calcium carbonate he was able to filter 30 cubic feet per hour under 10 lbs. per square inch pressure. The adhering oil broke loose from the filtering surface and floated to surface. The permeability of the filter was

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but slightly dimished after 6 hours filtration. He advises using the calcium carbonate in a filter press at not higher than 50 lbs. pressure because higher pressures squeeze the emulsified oil drops between the interstices in the filter bed.

This method worked also for emulsions of kerosene, petroleum oils, fatty oils, etc., where soap or saponin had been used as emulsifiers.

He also mentions that addition of alum and alkali, and also passing oily water between iron electrodes between which a current is passing, works well. Ferric oxide is formed at the anodes and combines with the oil particles and coagulates them. These methods are limited for commercial use.

For laboratory purposes, Hatschek recommends the ultrafilter using Bechhold's 5% collodion papers as highly satisfactory.

In 1911 Hatschek (Koll. Zts., **9**, 159) tried hydrochloric acid and sodium sulphate as coagulators. At, or near, the isoelectric point the particles did coalesce to form larger ones (about 3 microns diameter) but oil particles of even this size rise very slowly—about 2 cm. in 48 hours.

Ellis (Z. Physik. Chem., **80**, 597 (1912)) showed that these emulsions are most stable in presence of N/1000 NaOH and least stable in presence of, — $AlCl_3$ — 0.00022 gm. molar
$CuCl_2$ — 0.004 " "
NaCl — 0.16 " "

Powis (Z. Phys. Chem. **89**, 186 (1914)) showed that greatest instability of these emulsions was attained when the contact potential reached ±0.03 volt. This potential was found in the presence of, — KCl — 51 millimolar
$BaCl_2$ — 1.9 "
$AlCl_3$ — 0.02 "
$ThCl_4$ — 0.007 "

A slight increase over these concentration charges the particles with positive electricity and they become stable again.

In 1914, Ellis (Z. Physik. Chem. **89**, 145) showed that colloidal ferric hydroxide from 0.0017 to 0.0039% final concentration coagulates this type of emulsion. Higher concentration results in reversal in charge of the dispersed phase and stability.

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Philip (J. S. C. I. **34,** 697 (1915)) advised that the emulsification tendencies of a lubricant be tested before using. He found that very slight contamination of a good non-emulsifying mineral oil by Mexican, Trinidad or Persian crude oils greatly increased the tendency to emulsify. He described a test for the purpose.

Harris, (U. S. Patent 1281952 (1919)) proposes to break emulsions of water and petroleum oil by passing heavy electrical current through. The electrodes must be close together.

Dijxhoom (Le Papier **22,** 53 (1919)) removes emulsified lubricating oil from condenser water by passing 110 volt current through water as it passes through feed water pipe.

Rogers, (U. S. Patent 1,299,835 (1919)) breaks emulsions of mineral oil and water by adding sodium salt of a sulphonated mineral oil (¼ to 4 lbs.) per barrel of mixture and heating.

McKibben (U. S. Patent 1,299,589 and 1,299,590 (1919)) passes emulsion of petroleum and water (heated sufficiently to produce vaporization) through an intensified electrical field. The vapors are condensed and cooled and the water drops out.

McNear and Bowles (U. S. Patent 1,297,378 (1919)) patent an apparatus for electrical treatment of emulsions.

Successful attempts have been made to precipitate emulsified water in linseed oil, etc., by high tension electrical discharge. There are certain difficulties to overcome. The sparks sometimes tend to jump over the surface rather than through the mixture.

Pilat and Piotrowski (Petroleum, **13,** 1045 (1918)) favor heat treatment under pressure for breaking crude petroleum emulsions consisting of oil, salt water and earthy matter. By heating in closed kettles (capacity 40,000 kg.) with steam at 3 to 3½ atmospheres pressure at 120°-130° C., practically quantitative separation was accomplished. At 3 atmospheres pressure it took place in five hours. At higher pressure the separation takes place more quickly.

Koetschau (Z. angew. Chem. **32,** 45 (1919)) claims heating Roumanian and Galician petroleums breaks the emulsions. He recommends heating acidified distillates with steam at 3-4 atmospheres pressure.

Newman (J. Phys. Chem. **18,** 34 (1914) found that emulsions of oil in water with soap as emulsifying agent are irreversibly broken by freezing.

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One could continue indefinitely discussing special means of breaking emulsions, but from a knowledge of the nature of a given emulsion and application of the principles laid down at the head of this chapter, one ought to be able to deal with each special case.

Since foams are closely related to emulsions it is of interest to note here that Fiske (J. Biol. Chem., **35**, 411 (1918)) has found isoamyl valerate to be an excellent inhibitor of foaming. He describes methods for preparation of this ester.

Columbia University,
New York City.

THE SHAKE METHOD AND FILTER METHOD IN THE ANALYSIS OF TANNING MATERIALS WITH HIDE POWDER.

By G. Baldracco and S. Camilla.

(Translated from *J. Soc. Leather Trades Chemists III*, 110 (1919).).

Although adopted as official by the International Association of Leather Trades Chemists, the Shake Method[1] has never been in favor among analysts because of the long and complicated procedure required. During the discussion of the method at the International Congress of Leather Trades Chemists at Brussells in 1908, one of us made certain recommendations with the object of making the filtration and washing of the chromed hide powder simpler and more rapid.

In spite of official instructions to use the Shake Method, the Filter Method has been practiced upon a large scale, especially in Italy, by the manufacturers of tanning extracts, using the lightly chromed powder prepared by the *German Experiment Station for the Leather Industry*. When the war broke out, the hide powder prepared at Freiburg was no longer available, and, after some study and experimenting, a hide powder was prepared here at the *Royal Institute for the Leather Industry* (Turin, Italy) equal to that made at Freiburg, which had been considered by the majority of analysts as best for use with the Filter Method. Nu-

[1] **Translator's Note: Detailed descriptions of both the Shake and Filter methods are given in *Procter's Leather Industries Laboratory Book*, Sections XII and XIII. The present article assumes familiarity with both methods.**

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merous analyses were made of various types of extracts and tanning materials, using in each case both the Freiburg powder and that prepared here; the results were always concordant. Having made certain that our hide powder was fully equal to that which analysts had considered best for the Filter Method, we set out to elucidate the much discussed, though never completely settled question of the superiority in accuracy of the official Shake Method over the Filter Method.

In the analysis of tanning materials, it is well known that the Filter Method always gives higher results for tannin, for certain materials very much higher, than are obtained by the Shake Method. The discrepancies between the results by the two methods have been attributed to the property of hide powder in removing non-tannins from solution. Our research had the double purpose of proving irrefutably the superiority of one method over the other and making it clear to the analyst how to combine accuracy with ease of manipulation.

Reasons for the Inaccuracy of the Filter Method.—The data obtained by the two methods have been discussed in numerous publications, but in spite of the recognized defect of the Filter Method, the absorption of non-tannins by the hide powder, no one has attempted an efficient demonstration of this defect[2]. With this object in view, we have made a scrupulous examination of the non-tannin filtrates obtained by the two methods.

Among the non-tannins which interest us most, because they are absorbed by hide powder, are the alteration and decomposition products of the tannins themselves. Indeed there are two such products often found in non-tannin filtrates, namely, gallic acid and pyrocatechin. After confirming the presence of these or similar substances, it is necessary to get some idea of the relative amounts in non-tannin filtrates by the two methods. If the filtrate contains little or none of these substances which are known to be present in the original material, then it is evident that they must have been absorbed by the hide powder and the method is therefore not as accurate as it should be.

Experiments with pure solutions of gallic acid and pyrocatechin are not conclusive because, in employing these solutions with

[2] Attention should be directed to the very comprehensive article on this subject by H. C. Reed. This JOURNAL 1, 288 (1906).

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either method, conditions are obtained not sufficiently like those in the case of tan liquors to enable one to draw absolute conclusions. In tanning materials and extracts these non-tannins are presumably in a state of combination and of a constitution different from the chemically pure substances. It was therefore necessary to find sensitive means of estimating gallic acid, pyrocatechin, and similar substances in the non-tannin filtrates obtained by the two methods for the same tan liquor.

We therefore carried out a series of experiments using the most delicate tests known for gallic acid and pyrocatechin and finally decided, as the best procedure, to base our conclusions upon the reactions between non-tannin filtrates and the following reagents:

(a) A very dilute solution of ferric chloride ((about 0.5%).

(b) A 2% solution of ammoniacal nickel sulphate, added drop by drop, followed by shaking, heating to boiling, and then by the addition of an excess of ammonia.

(c) A few drops of a 4% solution of formaldehyde followed by the careful addition of concentrated sulphuric acid to prevent mixing, thus permitting the observance of a colored ring at the boundary of the two liquids.

These reagents were first tried with pure solutions of gallic acid, pyrocatechin, phloroglucinol, and tannic acid. In Table I are given the results obtained using 3 drops of ferric chloride, 3 of ammoniacal nickel sulphate, and 3 of formaldehyde solution to 5 cc. portions of 0.05% solutions of gallic acid, pyrocatechin, and phloroglucinol, and 0.01% solution of tannic acid which is so dilute as to give only a faint milky appearance with the gelatine-salt reagent used to test non-tannin filtrates. According to Waage, phloroglucinol is a transformation product of tannin widely distributed throughout the vegetable kingdom wherever tannins are found.

The next step was to examine the effect of the presence of dissolved hide substance in the non-tannin filtrates upon the tests with the above reagents. The above tests were repeated but to each 5 cc. portion of solution was added one drop of the gelatine-

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TABLE I.

Reagent	Gallic acid	Pyrocatechin	Phloroglucinol	Tannic acid
Ferric chloride.	Solution dark blue, becoming decolorized after a time. No precipitate.	Solution emerald green. After a time a green precipitate separates, leaving solution nearly colorless.	Solution at first colorless, but after a time becomes slightly brownish yellow.	Solution dark blue. After a time a blue precipitate separates, leaving solution colorless.
Ammoniacal nickel sulfate in the cold, with shaking.	Solution at first red, then brownish, and continues to darken.	Solution at first colorless; after shaking, it turns a reddish brown.	Solution at first colorless, but becomes slightly opalescent.	Flocculent reddish precipitate; solution colorless.
The above after heating to boiling.	Solution turns green, brightens, and then becomes dull.	Solution at first milky white; then a flocculent brown precipitate separates and the solution becomes clear.	The opalescence becomes more pronounced and finally a dirty white precipitate separates.	Precipitate turns a greenish brown; solution remains colorless.
The above upon adding an excess of ammonia after heating.	Green solution becomes clearer.	Precipitate redissolves and solution becomes a clear yellow.	Precipitate slowly redissolves and upon cooling gives a violet-rose solution.	Precipitate becomes a darker brown, solution remains colorless.
Formaldehyde solution and concentrated sulfuric acid.	No colored ring at interface, nor any turbidity. Upon shaking, the mixture becomes red; after an hour numerous bubbles of gas appear and a fine rose colored precipitate separates.	Beautiful violet ring is formed at interface, while the solution just above becomes milky white. Upon shaking, a dark violet precipitate forms, leaving a violet colored solution, but this color disappears with the complete separation of precipitate upon cooling.	Orange yellow ring at interface with opalescence of solution just above. Upon shaking, orange colored precipitate separates; solution colorless.	No colored ring at interface; after 10 to 20 minutes solution just above becomes opalescent. Solution at first colorless after shaking, but turns after an hour to a light rose color.

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salt solution before adding the reagent. The effect of the reagents upon gelatine alone was determined by adding one drop of gelatine-salt solution to 5 cc. of pure water and then carrying out the tests as with the non-tannins. The results follow:

(a) With ferric chloride, neither coloration nor precipitate.

(b) With ammoniacal nickel sulfate in the cold and with shaking, a flocculent precipitate is formed which becomes more pronounced upon heating and which is not redissolved by a slight excess of ammonia.

(c) With formaldehyde solution and sulphuric acid, no colored ring is formed at the interface, nor is there any coloration in the solution.

In the case of the 0.01% tannic acid containing gelatine, all tests gave the same results as though no gelatine were present. With 0.05% gallic acid containing gelatine, upon the addition of 3 drops of ferric chloride reagent, the solution at first becomes blue, but soon a bluish grey precipitate separates; with gallic acid free from gelatine, while the color fades, the solution remains clear. The 0.05% solutions of pyrocatechin and phloroglucinol react the same whether gelatine is present or not.

The several tests were then applied to the non-tannin filtrates from both the Filter Method and Shake Method in the analyses of samples of the chief tanning materials and extracts in common use. The results are given in Table II.

It is our intention to extend these tests to other tanning materials not so commonly used; this will be taken up in another paper in which we intend to characterize the different extracts employed in the tannery.

We are now in a position to make the important deduction that in the Filter Method a large part, in some cases all, of those non-tannins which are decomposition products of the tannins are retained by the hide powder. This completely confirms the reason formerly given as to the cause for the discrepancies between the results of the two methods in the determination of tannin. We should point out further that the non-tannin filtrates from the Filter Method contain dissolved hide substance. This is confirmed by the precipitate which is always formed in the filtrates

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TABLE II.

Reagent	Non-tannin filtrate from					
	Liquid chestnut extract		Liquid sumac extract		Dry mangrove extract	
	Filter method	Shake method	Filter method	Shake method	Filter method	Shake method
Ferric chloride.	Solution assumes a very light and fugitive greyish blue tint.	Clear blue solution, unchanged by time.	Intense violet blue coloration followed later by blue precipitate, leaving solution still colored, although brighter.	Very intense violet blue solution; no precipitate.	Clear green solution, becoming slightly decolorized.	Dark green solution which becomes decolorized by separation of a flocculent greenish brown precipitate.
Ammoniacal nickel sulfate in the cold, with shaking.	Solution colorless; dirty greenish white precipitate separates.	Red solution, becoming darker upon shaking, but remaining clear.	Red solution becoming reddish brown upon shaking.	Golden yellow solution, becoming dark olive upon shaking.	Colorless opalescent solution with a dirty, brown flocculent precipitate.	Yellow solution, becoming reddish, opalescent, and then decolorized, giving a red precipitate.
The above after heating to boiling.	Precipitate becomes clotted and more pronounced; solution colorless.	Solution turns greenish and brightens; still clear.	Solution greenish, later turning reddish.	Solution darkens still more.	Precipitate becomes clotted and more pronounced, assuming a light reddish tint.	Precipitate becomes more pronounced, solution still clear.
The above upon adding a slight excess of ammonia.	Precipitate does not redissolve, but becomes a dirtier green, solution clear.	Solution clear and of same color only brighter.	Solution becomes light olive.	Solution nearly decolorized.	No change.	Precipitate partly redissolves, leaving a reddish brown precipitate in a red solution.
Formaldehyde solution and sulfuric acid.	Very light reddish brown ring at interface. Upon shaking, mixture becomes a rather dull reddish brown.	Very pronounced reddish brown ring at interface. Upon shaking, mixture becomes an intense red.	Reddish brown ring at interface Upon shaking, mixture becomes reddish brown; no precipitate.	Reddish brown ring at interface with solution just above opalescent and of a golden yellow color. Upon shaking, mixture becomes reddish brown; later brown precipitate separates leaving solution clear.	Light red ring at interface with clear yellow solution above. Upon shaking, mixture becomes reddish brown. After cooling, reddish brown precipitate separates.	Very pronounced violet-red ring at interface with yellow opalescent solution above. After shaking, mixture becomes violet red and opalescent; later a reddish brown precipitate separates.

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TABLE II.—(Continued)

Reagent	Non-tannin filtrate from			
	Sulfited liquid quebracho extract		Cube gambier	
	Filter method	Shake method	Filter method.	Shake method
Ferric chloride.	Clear colorless solution.	Solution at first bluish, then greenish yellow and opalescent; later a light yellow precipitate separates.	Light greenish solution.	Intensely green solution followed by a green precipitate.
Ammoniacal nickel sulfate in the cold, with shaking.	Colorless solution, with precipitate.	Bright yellow solution with color becoming more pronounced; clear.	Greenish yellow solution with precipitate.	Clear golden yellow solution, becoming orange, and then continuing to darken.
The above after heating to boiling.	Precipitate becomes clotted.	Yellow color fades and solution becomes opalescent.	Greenish yellow precipitate becomes clotted.	Solution becomes orange yellow and slightly opalescent.
The above upon adding a slight excess of ammonia after heating.	Precipitate does not redissolve.	Color and opalescence persist for a long time, but finally solution clears and turns reddish brown.	Precipitate merely darkens.	Solution turns clear light brown; darkens later.
Formaldehyde solution and sulfuric acid.	No colored ring at interface. Upon shaking, mixture becomes clear brown; after several hours a very light brownish precipitate separates.	Violet-red ring at interface with solution above opalescent. Upon shaking, solution becomes rose colored; later it becomes decolorized and flocculent rose colored precipitate separates.	Brown ring at interface with yellow opalescent solution above. Solution becomes brownish yellow upon shaking.	Pronounced brownish red ring at interface, with strong greenish white opalescence in solution above. Abundant violet precipitate separates upon shaking, leaving red solution.

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tested with nickel sulfate, and also by the test with ferric chloride which form a precipitate in the presence of gallic acid if the solution contains any dissolved hide substance. The dissolving of hide substance in the Filter Method was confirmed in a much better manner, however, by determining the nitrogen both in the precipitates and in the non-tannin residues.

Another fact worthy of remark is that if tan liquor in excess of 90 cc. be passed through the hide powder in the filter bell, the non-tannin filtrate, although it gives no precipitate with gelatine, then contains appreciable quantities of those non-tannins which we have examined particularly. This shows that these decomposition products of the tannins are held only loosely by the hide, a fact which can be verified in those cases where the filtration is carried on much more slowly than usual.

The results given in Table III show very clearly the discrepancies between the two methods in the actual analysis of tanning extracts. The disagreement is very pronounced in cases where the extract contains a large proportion of those non-tannins which are decomposition products of the tannins themselves, as for example in gambier extract, which we have very properly taken into consideration, even though its use in the tannery is relatively limited. Gambier extract contains a large quantity of pyrocatechin, which the hide powder in the Filter Method absorbs to a great extent, so that the use of this method in the analysis of gambier results in a remarkably large error, when investigating the tanning value of this material.

Necessity for Modifying the Shake Method to Make It More Practical and Expeditious as well as Absolutely Accurate.—The disadvantages of the Shake Method are well known and justify in a large measure the aversion to its adoption. The chroming of the hide powder, the washing of which has been called by Hough the black beast of the Shake Method, requires a great expenditure of time and labor. The adding of a definite quantity of water to the hide powder, which must be suitably washed and pressed, before proceeding with the shaking with the tan liquor, although done carefully, can easily lead to errors which are practically unavoidable. This is why there is such an aversion to the official method and why in general it is used only upon the special demand of the client.

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But, since the superiority of the Shake Method has been confirmed and demonstrated as to its absolute and unquestionable accuracy, it was only logical that we should make every effort to find means of eliminating the disadvantages of the method, making it more practical as everyone desires, more rapid of execution and at the same time rigorously accurate.

In this *Institute* we have already succeeded in preparing a hide powder equal to the best previously available and have decided to use it for analyses by the Shake Method. Although we have taken into account the failure of others in trying to establish the use with the Shake Method of a lightly chromed powder previously prepared, the method we are about to describe appears to us, after several trials, to be both easy and certain. So far as the washing of the hide powder is concerned, this method resembles the Filter Method, while for the determination of tannin it involves the same conditions of analysis as the Shake Method.

The Modified Shake Method.—For tanning extracts or materials to be extracted, such as leaves, barks, woods, etc., make up the solution for analysis in the same manner and with the same quantity of material as prescribed in the regular procedure. Start the analysis as for the Filter Method by passing through the filter bell, containing 8 to 10 grams of lightly chromed hide powder, 30 to 35 cc. of the tan liquor to be analyzed, in order to wash the hide powder. Then take off the filter bell, allow it to drain for a moment, and, by blowing through the narrow end, force the hide powder into the receptacle for shaking. Then add about 70 cc. of the tan liquor and shake for 15 minutes in the usual manner for the Shake Method. Then filter, first through a linen cloth, pressing out the greater portion of liquor, and then through a folded paper. It is not necessary to add kaolin, because the filtration is rapid without, and the filtrate always clear. By evaporating 50 cc. of the filtrate in the usual manner, one obtains the non-tannins contained in 50 cc. of the tan liquor.

The Shake Method thus modified requires much less time for its execution than the official method and even less than is normally required by the Filter Method. The results obtained by this modified method are practically identical with those obtained by the official method, taking the mean of two determinations in each case, as is shown by the results given in Table IV.

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TABLE III.

	Liquid chestnut extract		Sulfited liquid chestnut extract		Dry chestnut extract		Sumac leaves		Liquid sumac extract	
	Filter method	Shake method	Filter method	Shake method	Filter method	Shake method	Filter method	Shake method	Filter method	Shake method
Tannin	38.09	34.38	28.94	26.11	68.24	60.93	9.88	6.68	25.23	20.02
Non-tannins	9.95	13.66	10.11	12.94	16.90	24.21	12.96	16.16	17.67	22.88
Insolubles	1.56	1.56	0.26	0.26	1.86	1.86	67.89	67.89	1.40	1.40
Water	50.40	50.40	60.69	60.69	13.00	13.00	9.27	9.27	55.70	55.70
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

	Sulfited liquid quebracho extract		Dry quebracho extract		Dry mangrove extract		Cube gambier	
	Filter method	Shake method	Filter method	Shake method	Filter method	Shake method	Filter method	Shake method
Tannin	31.42	30.18	71.56	69.26	51.55	48.55	53.81	45.18
Non-tannins	6.94	8.18	15.60	17.90	25.17	28.17	16.85	25.48
Insolubles	0.55	0.55	0.39	0.39	5.53	5.53	18.05	18.05
Water	61.09	61.09	12.45	12.45	17.75	17.75	11.29	11.29
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

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TABLE IV.

	Liquid chestnut extract		Sulfited liquid chestnut extract		Dry chestnut extract	
	Official method	Modified method	Official method	Modified method	Official method	Modified method
Tannin	34.38	34.24	26.11	26.23	60.93	60.77
Non-tannins	13.66	13.80	12.94	12.82	24.21	24.37

	Sumac leaves		Liquid sumac extract		Dry mangrove extract	
	Official method	Modified method	Official method	Modified method	Official method	Modified method
Tannin	6.68	6.45	20.02	19.89	48.55	48.32
Non-tannins	16.16	16.39	22.88	23.01	28.17	28.40

	Sulfited liquid quebracho extract		Dry quebracho extract		Cube gambier	
	Official method	Modified method	Official method	Modified method	Official method	Modified method
Tannin	30.18	29.94	69.26	69.61	45.18	45.54
Non-tannins	8.18	8.42	17.90	17.55	25.48	25.18

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In the analyses by the official method we have used the non-chromed hide powder prepared by the *German Station for the Leather Industry* of Freiburg. Perfectly concordant results are also obtained when using the non-chromed hide powder prepared at this *Institute*.

Conclusion.—By the facts which we have just described, we hope to have demonstrated that the Shake Method is the accurate method for the determination of tannin in extracts and tanning materials.

In order to make this determination more expeditious and easier of execution without impairing its accuracy, we propose the modification of the Shake Method in the direction we have indicated and ask that it be submitted for official approval.

NATIONAL ROYAL INSTITUTE FOR THE LEATHER INDUSTRY, Turin, Italy.

J. A. W.

ABSTRACTS.

The Molecular Mechanism of Colloidal Behavior. II. The Swelling of Fibrin in Alkalies. By R. C. TOLMAN and R. S. BRACEWELL, *J. A. C. S.* **41**, 1503 (1919). Experiments on the swelling of fibrin in alkaline solutions, similar to those performed previously with acid [abst. JOURNAL 13, 131 (1918)]. Owing to amphoteric nature of the amino acids of fibrin, it has a tendency to absorb hydroyl-ions just as it does hydrogen ions, and hence the phenomena are the same in both solutions. The authors conclude that the behavior of fibrin in solutions of strong alkali and ammonia, also with addition of neutral salts is similar to the behavior in strong acid solutions and can be explained by the same theory.

The Molecular Mechanism of Colloidal Behavior. III. The Chemical Nature of the Adsorption of Acids and Alkalies by the Protein Molecule. By R. S. BRACEWELL. *J. A. C. S.* **41**, 1511 (1919). The results of the two articles referred to above are discussed on the basis of recent ideas of adsorption which attribute the attractive to stray fields of chemical force around the atoms whose affinity has not been fully satisfied, and consider the adsorptive affinity as a chemical force. The experiments showed that there was a definite maximum adsorption of alkali or acid from solution which is not increased by considerable increase in the concentration of the solution, which indicates that there may be a limited number of positions on the protein molecule where hydroxyl or hydrogen ions tend to attach themselves, and that after these positions are saturated the protein molecule has become electrically charged to such a degree that further "indiscriminate" adsorption does not take place. The amount of

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acid "neutralized" by a considerable number of proteins appears to be determined by the number of free amino groups in the molecule. The adsorption of hydroxyl ions by protein is of a less specific character, in general it seems that proteins' high affinity for alkalies are high in simple straight-chained amino acids.

The Proximate Analysis of Commercial Casein. By F. L. BROWNE, *J. I. T. E. C.* **11**, 1019 (1919). The methods for the analysis of casein as used by the Forest Products Laboratory of the U. S. Forest Service for its valuation for use in waterproof glues. These are as follows:

Color. Commercial casein may be obtained which is almost pure white, and the color need never be more than a pale yellow or cream.

Odor. Commercial casein may be obtained which is entirely free from odor, or, at most, has an odor resembling sweet milk. The rancid odor frequently associated with casein is due to impurities or decomposition products. The odor is determined as follows: About 10 grams of casein are soaked in about 10 cc. of water and an equal volume of a rather thick milk of lime added with stirring. After the mixture has stood a few moments the odor is noted.

Fineness. A 50-gram sample is placed on a 60-mesh sieve, the sieve is held in one hand and move horizontally back and forth at the rate of about 120 strokes per min., being allowed at the end of each stroke to strike against the palm of the other hand. The portion passing through in 10 minutes is weighed, and reported as per cent. passing 60-mesh.

Moisture. Accurately determined by weighing out a 3-gram sample in a weighing bottle, heating to constant weight in a vacuum oven at 70 to 80° C., cooling in a dessicator and weighing. It is more convenient and sufficiently accurate to use a porcelain dish and make the determination by heating in a Freas oven at 98° C., and atmospheric pressure for five hours.

Fat. The residue from the moisture determination is transferred to an extraction thimble and extracted for 16 hours with anhydrous, redistilled, ethyl ether in a Cauldwell or Soxhlet apparatus. For practical purposes the extraction is complete in 8 hours.

Ash. A 3-grain sample is weighed out in a vittecosil dish and carefully charred over the low flame of a Bunsen burner. When completely carbonized it is placed in an electric muffle furnace and heated at a dull red heat (not over 600° C.) until the ash is white or at least light gray, and the weight is constant. A small amount of ammonium nitrate made be added to facilitate the combustion of the last traces of carbon.

Nitrogen. A one-half gram sample is weighed into an 800 cc. Kjeldahl flask, 20 cc. of concentrated sulphuric acid, 10 grains of crystallized sodium sulphate, and a small crystal of copper sulphate are added and the contents digested until a clear solution is obtained and then for 30 minutes longer. 300 cc. of distilled water, 50 cc. of a 1:1 solution of sodium hydroxide, and about ¼ gram of granulated zinc are added. About 250 cc.

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are then distilled over and caught in standard sulphuric or hydrochloric acid (30 cc. N/5 acid will be sufficient). The excess acid is back-titrated with standard sodium hydroxide solution, methyl red being used as indicator. Nitrogen results are reported on a moisture-, fat-, and ash-free basis.

Acidity. A 1-gram sample is placed in a flask and 25 cc. of N/10 sodium hydroxide solution run in from a pipette. The flask is stoppered and agitation continued until solution is complete. 100 cc. of water (neutral to phenolphthalein) are then added and the solution titrated at once with N/10 acid, using 0.5 cc. of alcoholic phenolphthalein solution. The number of cc. of N/10 alkali used up by 1 g. of moisture-, fat-, and ash-free casein is called the "acidity" of the sample. The following precautions must be observed if this method is to give concordant results: (1) The flask should be kept stoppered except when making additions or titrating; (2) the amount of indicator specified must be used and it must be adjusted so that 1 drop added to distilled water does not change its reaction; (3) local coagulation of casein during titration must be avoided; (4) the total time during which the casein is allowed to stand in contact with the alkali must not exceed 30 minutes at room temperature.

Government specifications require that all casein should pass the following tests:

Color. White or light cream.
Odor. Nearly odorless, with not more than a trace of sourness.
Moisture. Not more than 10%.
Fat. Not more than 1%.
Ash. Not more than 4%.
Nitrogen. Not less than 14.25%.
Acidity. Not more than 10.5 cc. N/10 alkali per gram.

Oil [Chamois Leather] Tannage. W. MÖLLER, *Collegium*, 1919, 61–72. *Chem. Zentr.*, 1919, **90**, IV., 52–53. Tanning experiments with mixtures of fish-oils or dégras and phenols indicate that in the case of oil tannage also the author's "peptisation theory" holds good, the phenols acting as peptising agents (this J., 11, 592). The oxidised fish-oil itself has tanning properties, and therefore Fahrion's view (Neuere Gerbetheorien u. Gerbmethode, p. 48) that tannage is effected only by nascent fatty acids derived from the oxidised oil, is incorrect. In tanning with mixtures of dégras (but not fish-oil) and phenols water is liberated in proportion to the amount of these substances taken up by the skin, and the author concludes that oxidation of the fish-oil is conditioned by the water present in the skin. Oleic and stearic acids also tan in presence of phenols, but the character of the product resembles that of ordinary leathers rather than chamois leather.

Hydrocarbon Tannage. W. MÖLLER, *Collegium*, 1919, 72–82. *Chem. Zentr.*, 1919, **90**, IV., 53. Mixtures of phenols with mineral oil or with the acid resin—consisting mainly of hydrocarbons—obtained in accordance

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with Ger. Pat. 262,333, have a tanning action on pelt, producing a leather similar to that obtained in the author's experiments on the chamois leather tannage (see preceding abstract). The presence of active groups (*e g.*, .OH,COOH) in the molecule of the tanning agent is therefore not essential.

The Tannins of the Acacia. By W. MÖLLER, *Gerber*, **44**, 105. An investigation on the tannins of the black locust or false acacia (*robinia psuedoacacia*). Small quantities of this acacia-wood extract was produced by a German extract manufacturer in the last year of the war. Analysis of the tree for tannin content yielded the following results:

	Young Trees		Old Trees	
	Bark	Wood	Bark	Wood
Tannin	2.2%	4.0%	7.2%	3.4%
Non-tannin	6.4	2.2	4.5	2.1
Insoluble	59.0	56 9	78.3	80.6
Water	32.4	36.9	10.0	13.9

Newly felled wood yielded 4.1% bark, 3.4% bast, 27.5% sapwood and 65% heartwood. Analyses of these separate parts gave the following results:

	Bark	Heartwood	Bast	Sapwood
Tannin	4.1%	4.7%	12.8%*	1.0%*
Non-tannin	3.6	1.8	8.2	3.6
Insoluble	81.3	61.8	57.0	72.0
Water	11.0	25.7	25.7	23.4

* Designated as matter absorbed by hide. Bast and Sapwood are free from tannin.

The tannin of the bark is a pure protocatechol tannin, that of the heartwood is a mixture of protocatechol and pyrogallol tannin. The heartwood contains a yellow coloring matter which is extracted by water while the aqueous extract of the bark is free from this coloring matter.

The composition of some acacia wood extracts are given as follows:

Gravity Bé	22.8°	23.4°	23.6°
Tannin %	25.1	25.6	25.2
Non-tannin %	12.0	12.4	14.1
Insoluble %	2.8	2.6	2.2
Water %	60.1	59.4	58.5

Tanning experiments were made with this acacia wood extract and with oak wood extract for comparison. In general the acacia extract tanned through somewhat slower than the oak. The former does not ferment as easily as the latter and imparts a light yellow color to the leather on account of the coloring matter it contains. It can be used to advantage in mixtures with other tanning extracts but its exclusive use is not to be considered because the crystalline nature of the considerable quantity of coloring matter, which it contains, produces a somewhat brittle leather. G. W. S.

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Tannin Analysis. By J. JEDLICKA, *Gerber*, **44**, 317; **45**, 2 & 14. An investigation of the proposals made by Bennett[1] for preventing high tannin results which are usually called the "personal factor." According to Bennett the causes are:

1. Insufficient drying of the residue, especially of the total soluble.
2. Drying oven not functioning well.
3. Fluctuating strength of solutions used (0.35-0.45% tannin).
4. Cooling the dishes in too short a time.

To lessen the error due to the "personal factor" Bennett proposes:

a. For the determination of total and soluble solids only 25 cc. of the solution be used.

b. To facilitate the removal of the volatile acids by adding to the solution to be evaporated, 0.5 cc. of a 0.5% solution of tartaric acid and subtracting 25 mmg. from the result.

c. To let the dishes cool the same length of time, at least an hour, before weighing.

d. To fix a closer limit than 0.35-0.45% for the tannin content of the analytical solution.

The author treats each proposal in the order given.

Twelve comparative evaporations, using 50 and 25 cc. of the same solution of oak extract, were made, and by drying 25 cc. on an average of 0.1% more of soluble solids was obtained than in drying 50 cc.

The addition of 25 mmg. of tartaric acid to 50 cc. of the total soluble before evaporating, yielded a residue that was 0.74% (average of 12 tests) lower than without the addition. Tartaric acid was also added to the non-tannin solution before evaporating and a similar loss was obtained. It therefore appears that the source of the loss in weight, due to the addition of tartaric acid, is in the non-tannins. The loss increases with increasing amount of tartaric acid until a maximum loss of 34% of the non-tannins was obtained. The residue obtained was black, and more difficultly soluble than those not treated with tartaric acid. It was assumed that the pentoses present in the extract were changed, under the influence of tartaric acid, into furfurol, but tests did not confirm the assumption as only traces were found. It is possible that a decomposition of the potassium salts, which are present in the non-tannins of oak wood extract, occurs. It is the author's experience that the mineral constituents in the non-tannins of oak wood extracts undergo great changes, for example, an extract that contained 3.30% ash, by direct ashing, when ashing the non-tannin residue yielded 12.98%.

The proper cooling of dishes is a recognized essential. In the author's laboratory, weighing is started after 20 minutes and the work requires from 25-30 minutes, so that the last dish is cooled 45 minutes. The empty dishes, after being dried first in the oven, are weighed in the same order and the same manner. Nevertheless variations in the weight of empty dishes occur unless they are left to stand in the balance for 15 minutes before weighing. This is a practical impossibility in tannin analy-

[1] *London Coll.* 1915, 97.

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sis and the author sees no necessity for lengthening the processes any more for such a slight variation in results, and suggests the starting point be exactly prescribed, for example, "exactly after 20 minutes" (instead of at least 20 minutes).

In order to obtain correct results, *i. e.*, according to Bennett's point of view—the lowest possible per cent. of tannin—he employs a solution containing 0.35% tannin. This would not be objected to by the extract producers, who could more easily obtain the proper concentration from their knowledge of the raw materials and method of manufacture. But it would be decidedly unfair to the other analysts as it would mean a preliminary analysis and a lengthening of a process that is already sufficiently time-consuming. However, even the extract producers have difficulties in excluding fluctuations, as is shown from the author's results on 288 samples of liquid oakwood extract (37° Bé), only 91% of the solutions were within the limits of 0.37-0.41%. The mean of all analyses gave a strength of 0.39%. It is the duty of all conscientious analysts to approximate 0.4%, but a sufficient latitude must exist.

To summarize—the deviations from the official shake method employed by Bennett are not expedient and therefore not to be introduced. An addition of tartaric acid to the solutions before evaporating is to be unconditionally rejected. G. W. S.

PATENTS.

Treating Leather. British Patent 132,807. O. ROHM, Darmstadt, Germany. Chrome leather after leaving the chrome bath is treated with a basic solution to neutralize it, the solution being formed of mixtures of carbonates of alkalis or alkaline earths with formaldehyde, or salts of the lower fatty acids, or oxy-fatty acids, *e.g.*, formates, acetates, or lactates. As examples of the process, 100 kilos of wet chrome leather are treated with 300 litres of water in which are dissolved either (*a*) 1 kilo of soda and 0.5 kilos of formaldehyde, or (*b*) 1 kilo each of calcium of carbonate and sodium formate.

Chromium Salts; Tanning. British Patent 131,772. J. R. BLOCKEY and W. WALKER & SONS, Bolton, Lancashire. Sept. 28, 1918. Chrome liquors and salts for use in tanning are made by acidulating bichromate with sulphuric or hydrochloric acid and reducing the compound so as to obtain trivalent salts, by the addition of waste tannery products such as spent tanning materials, waste chrome or vegetable leather, waste sludge from tan pits, either wet or dry, or the dust from tanning material extraction plant.

Leather Working and Like Machines. British Patent 132,843. A. SEYMOUR JONES, Pendower, Wrexham and Haley & Co., Bramley, near Leeds. Sept. 6, 1918.

Relates to yielding work-supports for leather-working and like machines.

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Detanning Chrome Leather; Glue &c. British Patent 132,864. M. C. LAMB, London. Sept. 24, 1918. Chrome leather is detanned and the material used for making glue or gelatine. The chrome leather is immersed in a solution of an organic acid containing two or more hydroxyl groups. Suitable acids are phthalic, lactic, tartaric, succinic, malonic, and oxalic, preferably the last-named. The chromium is recovered from the solution and the detanned material treated in the usual way for making glue, &c.

Machine for Leather Flexing and Tempering. U. S. Patent 1,313,510. WALLACE C. WRIGHT, Lynn, Mass. Sept. 26, 1916. A leather tempering machine having mechanism to moisten, to convey, and to undulate a leather blank in combination with means to vary the undulating action.

Pyroxylin Composition and Process of Making Same. U. S. Patent 1,320,458. WILLIAM F. DOERFLINGER, Staten Island, N.Y. Dec. 6, 1918. As a new composition of matter, a coating composition comprising a non-drying oil and pyroxylin dissolved in a volatile solvent containing diacetone alcohol, normal butyl alcohol, a volatile ketone, and benzol.

Tanning Leather for Belts. U. S. Patent 1,321,730. FELICE GILARDINI, Turin, Italy. May 21, 1918. A method of manufacturing leather which comprises subjecting portions of the unprepared hide to heated compressing elements, and subjecting the hide to a tanning solution.

Tanning Compound. U. S. Patent 1,323,878. BERTRAM LEVIN, Hale, England. May 28, 1918. As a new article of manufacture a salt of a metallopyrophosphoric acid containing boron as a part of the acid radical, which article is a solid less hygroscopic and less liable to revert to ordinary metallic phosphate than is the corresponding metallo-pyrophosphate.

Tanning Process. U. S. Patent 1,323,956. JOSEPH M. BROWN, Austin, Ark. Apr. 4, 1919. That method of tanning which consists in taking a quantity of water sufficient to cover a hide, dissolving cutch in the water in the proportion of one pound of cutch to ten pounds of hide, dipping the hide into said solution at successive intervals, adding to the solution powdered white vitriol of one-half the weight of the cutch, and returning the hide to the solution until completely tanned.

Method of Treating Varnished (Patent) Leather. U. S. Patent 1,325,415. HEINRICH SCHULZ, Worms, Germany. Dec. 12, 1916. The hereindescribed method of treating varnished leather, which consists in subjecting the leather to the action of light rich in ultraviolet rays in a closed chamber; and continuously forcing air, previously heated to a temperature above 40° Réaumur, into said chamber and exhausting it therefrom.

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CONTENTS

Elections - - - - - - - - 219
Notice - - - - - - - - - 220
Ballot on Proposal to Add to the Provisional Methods - - 221
Seventeenth Annual Meeting - - - - - - 221
Estimation of the Tryptic Activity of Bating Materials. By Arthur W. Thomas - - - - - - - - 221
The Swelling of Limed and Hydrated Hide in the Presence of Acid or Alkali. By George D. McLaughlin - - - 228
The Measurement of the Plumping Power of Solutions. By Alan A. Claflin. - - - - - - - - 234
Industrial Uses for the Shark and Porpoise. By Allen Rogers - 241
Abstracts - - - - - - - - 244

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John L. Wilson, 434 Somerville Ave., Philadelphia, Pa.

Louis J. Greenbaum, % J. Greenbaum Tanning Co., 2612-2628 Warsaw Ave., Chicago, Ill.

Samuel Greenbaum, % J. Greenbaum Tanning Co., 2612-2628 Warsaw Ave., Chicago, Ill.

Chas. Warren Dowd, 117 Eastern Ave., Lynn, Mass.

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NOTICE.

The official Hide Powder recognized by the American Leather Chemist Ass'n. is that prepared by the Standard Mfg. Co. of Ridgway, Pa. This company prepares each year a quantity approximately sufficient to supply the requirements for the following year and which is supplied to the users as 1918, 1919 Hide Powder, etc. The final stage in the preparation of the Hide Powder is grinding in a special mill. In former years the mill used by the Standard Mfg. Co. was of German manufacture. This mill gradually wore and during the preparation of the 1919 Hide Powder reached a condition such that it was no longer usable, a condition which resulted in a somewhat inferior preparation of the 1919 Hide Powder. It was impossible to secure parts or repair the mill and it therefore became necessary to purchase a new one of a different type. The selection of a suitable mill, the delay in delivery consumed so much time that it was with difficulty hide powder for 1920 could be made ready before the 1919 supply was exhausted, and no time was available for an extended study of the Hide Powder as prepared by the new mill.

The 1920 Hide Powder because of its superior preparation seems to detannize more efficiently than did the 1919 Hide Powder, which means that the 1920 Hide Powder shows an apparent higher percentage of tannin in a given material than is shown by the 1919 Hide Powder, the amount of the variation being under 1% as evidenced by results to date. This announcement is made to avoid possible confusion arising when a shift is made from the 1919 to 1920 Hide Powder. In order to avoid if possible a recurrence of a similar trouble the matter of the securing and maintenance of a uniform Hide Powder has been placed by the Council in the hands of a special Committee of the A. L. C. A. and it is by this Committee that this announcement is made.

March 10, 1920.

F. H. SMALL, *Chairman.*
C. C. SMOOT, III.
H. C. REED,
C. R. OBERFELL.

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BALLOT ON PROPOSAL TO ADD TO THE PROVISIONAL METHODS.

The ballot on the proposal to add to the Provisional Methods of the A. L. C. A. "Method for determining Oils, Fats and Waxes in Chrome-Tanned Leather, and in Combination Tanned Leather*," was as follows:—

Yes	23
No	13

According to the By-Laws, under 23, "if two-thirds of the members voting are in favor of the proposed method it shall become a provisional method of the Association." Thirty-six members voted, and in order to have this proposal passed, twenty-four should have voted yes. Therefore, this proposal failed to be adopted.

SEVENTEENTH ANNUAL MEETING.

The seventeenth annual meeting of the A. L. C. A. will be held at the Marlborough Blenheim, Atlantic City, N. J., on May 27, 28 and 29th.

Owing to the unusally crowded conditions at Atlantic City it is suggested that each member communicate direct with the management of the Marlborough Blenheim, as early as possible.

The schedule of rates is as follows:

	American plan per day	European plan per day
Single rooms without bath (one person)....	$8	$5
Single rooms with bath (one person).....	$10, $11, $12	$7, $8, $9
Double rooms without bath (two persons)...	$14	$7
Double rooms with bath (two persons).....	$16, $18, $21 to $25	$9, $11, $14 to $18

ESTIMATION OF THE TRYPTIC ACTIVITY OF BATING MATERIALS.

By Arthur W. Thomas.

Received March 10, 1920.

The wide use of preparations containing pancreatin (trypsin) in bates, of which "Oropon" is an example, requires a good method for the estimation of the activity of the enzyme contained therein.

* THIS JOURNAL, 14, 234 (1919).

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In general, such patent bating materials consist partly of the pancreatic trypsin and among other things, 60%—80% ammonium chloride. The need for estimation of the proteolytic activity of such products does not require discussion here. It has been difficult, however, to find a description of a reliable method. Many methods have been proposed but no one good procedure has been made available for the use of tannery chemists.

Dr. Dora E. Neun, working in this laboratory under the direction of Prof. Henry C. Sherman, has made a thorough investigation of methods of testing proteolytic activity of pepsin and of trypsin, the results of which were published in 1916[1].

The writer has selected two methods which Sherman and Neun found to be the best for estimation of the activity of trypsin and the procedures given herewith are taken directly from their original paper. These methods also prove to be the most reliable for the purpose of testing the tryptic power of commercial mixtures containing trypsin for bating.

The methods consist in allowing the enzyme to act upon a substrate of sodium caseinate at 40° C. In Method I, the nitrogen in the digestion products is determined by the Kjeldahl method, while in Method II, the digestion products are titrated to determine how much amino acid has been formed. For comparison of two specimens of trypsin either the amounts of nitrogen in, or acidity of, the digestion products caused by equal amounts of the enzyme at equal time intervals may be determined, or the lengths of time required for equal amounts of enzymes to form a given amount of soluble digestion products as measured by the nitrogen in, or acidity of, the digestion products may be adopted.

CASEIN SUBSTRATE FOR BOTH METHODS.

For trypsin digestions solutions of sodium caseinate, of the slight alkalinity best suited to tryptic activity, are prepared as follows:

Ten grams of casein are dissolved in a mixture of about 200 cc. of distilled water and 8 cc. of molar sodium hydroxide. The mixture is slowly heated to 40° C., to aid solution, and then rapidly heated to 85-90° to destroy any traces of proteolytic enzyme which might be contained in the casein. The solution is cooled and

[1] *J. Am. Chem. Soc.*, 38, 2199-2216.

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made up to 500 cc. For each determination, 50 cc. of this solution are placed in a 100 cc. flask, diluted to about 90 cc., warmed to 40° in a thermostat, the enzyme added, and the volume made up to 100 cc. During the digestion in the thermostat, the flasks should be protected from light since it has been found that light has a deteriorating influence upon the action of the enzyme. The enzyme action is stopped at stated intervals by pouring the digestion mixture (100 cc.) into 25 cc. of 20% sodium sulfate solution and then adding 5 cc. of half-molar hydrochloric acid. After standing for an hour, the undigested casein is filtered off and aliquot portions of the filtrate used for the measurements of proteolysis by one of the methods mentioned.

METHOD I. TOTAL NITROGEN OF THE DIGESTION PRODUCTS.

In the filtrate obtained after precipitation of the undigested casein by sodium sulfate and hydrochloric acid as described above, nitrogen can be readily determined by the Kjeldahl method and thus a measure obtained of the total of digestion products which have passed the early proteose stage. In using this as a method of studying proteolytic action of enzymes, "blank tests," in which all conditions and manipulations are the same except for the addition of the enzyme, must always be made and the nitrogen thus found deducted. The soluble nitrogen introduced with the enzyme preparation must also be allowed for. The figures given in the tables which follow are in all cases for the nitrogen found in the filtrates *in excess* of that found in the "blank". Table I shows the amounts of nitrogen digested by different weights of commercial trypsin (Trypsin I) acting for a fixed length of time. Table II shows the results of fixed weights of trypsins ((Trypsin I and Trypsin II) acting for different lengths of time.

The value of this method for quantitative comparisons is shown by the fact that, allowing for the probable errors of experiment, the amount of digested nitrogen compounds increases in direct proportion to the amount of enzyme used up to about 40-60 mg. of nitrogen, quantities large enough to be determined by the Kjeldahl method with a high degree of accuracy.

A comparison of the data for Trypsins I and II in Table II illustrates the importance of avoiding too long a time (or too large a quantity of enzyme) in making comparisons of enzyme activities. Trypsin I has about twice the activity of Trypsin II,

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TABLE I.—TOTAL NITROGEN OF DIGESTION PRODUCTS FORMED BY DIFFERENT WEIGHTS OF TRYPSIN ACTING UPON 1 GM. OF CASEIN IN A DIGESTION MIXTURE OF 100 CC. AT 40°.

	Half-hour digestions	20-hour digestions
Mg. of commercial enzyme	Trypsin I. Mg. of nitrogen digested	Trypsin I. Mg. of nitrogen digested
0.001	0.2	1.4
0.002	0.6	2.2
0.01	0.9	9.1
0.05	1.7	41.6
0.1	3.3	71.9
0.5	13.6	132.5
1	28.3	133.2
2	55.2	134.1
5	97.6	133.5
25	132.9	134.0
50	133.6	135.2
100	133.4	135.3

TABLE II.—TOTAL NITROGEN OF DIGESTION PRODUCTS.

Amounts of Nitrogen Formed in Different Times by 1 Milligram of Enzyme Acting on 1 Gram of Casein at 40°.

Time of digestion Hours	Trypsin I. Mg. of N. digested	Trypsin II. Mg. of N. digested	Apparent value of Trypsin I in percentage of that of Trypsin II as affected by time of digestion
½	36.1	16.6	217
1	61.4	32.0	192
2	98.4	59.5	165
3	119.1	81.9	145
4	128.4	100.3	128
6	133.4	120.2	111
8	135.8	128.4	106
21	138.4	136.5	101
48	138.0	136.4	101

as may be seen by comparing the amounts of total digested nitrogen for 30 minutes or for 1 hour of digestion. But when the digestion is too prolonged the product of the weaker enzymes steadily approaches that of the stronger until at the end of 8 hours the enzyme which really has twice the activity appears but little more active. If, on the other hand, the lengths of time required to digest a given amount of nitrogen are compared, it is found that, up to quite high amounts, the times required by Trypsins I and II are approximately as 1:2. This may be seen by reference to the data of Table II, or perhaps better, the curves in Figure I, from which it will be seen that the production of any given amount of total digested nitrogen (even up to 128 mg.) requires almost exactly twice as long with Trypsin II as with Trypsin I.

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Method II. Titration of Acid Cleavage Products (Volhard-Löhlein Method).

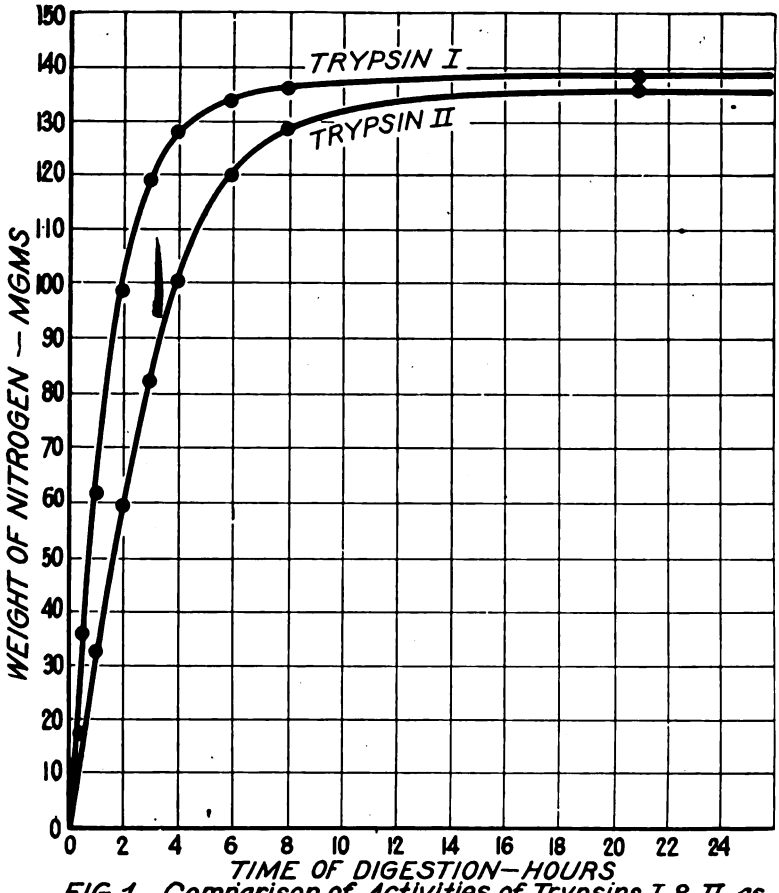

FIG. 1 – Comparison of Activities of Trypsins I & II, as measured by total nitrogen of digestion products

Thomas and Weber[1] estimated the activity of trypsin by allowing it to act upon casein as in the general procedure above described and weighing the undigested casein precipitated at the end of the digestion period. Volhard[2] tested pepsin, and Löhlein[3] trypsin,

[1] *Centrbl. f. Stoffw.-u. Verd.-Krankh.*, **2**, 365 (1901).
[2] *Biochem. Z.*, **2**, 231 (1903).
[3] *Beitr. Chem. Physiol.-Path.*, **7**, 120 (1905).

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by titrating the filtrate. This latter method has given promising results in the hands of Prof. Sherman and his students.

A portion of the filtrate (usually 50 cc.) is titrated with tenth molar sodium hydroxide using thymolphthalein as indicator. Thymolphthalèin is in nature like phenolphthalein but of different color change. In acid solutions it is colorless and in alkaline solutions it is deep blue.

The amount of alkali thus required, above that required in the "blank", depends upon the carboxyl groups of the digestion products plus a little of the hydrochloric acid used in the digestion or added with the sodium sulfate solution to precipitate the undigested casein; for the acidity of the "blank" filtrate does not account for all of the hydrochloric acid which has been added, indicating that some of it is held adsorbed in the undigested casein. The more complete the digestion of the casein, the less hydrochloric acid will it hold when precipitated at the end of the digestion period. In so far as this method depends upon the titration of carboxyl groups, it is particularly appropriate that it should accompany the use of casein as substrate on account of the high proportion of dibasic monamino acids which results from the hydrolysis of casein.

Tables III and IV show the results obtained by this method. The figures given (as in the preceding tables) are in all cases calculated for the total solution so as to indicate the work done by the amount of enzyme stated. Some of the filtrates were opalescent making the end point of the titration somewhat uncertain. In the cases of the commercial specimens used by Sherman and Neun it was possible to detect with certainty by this method an amount of enzyme as small as 0.01 mg., and usually as little as 0.002 mg. could be detected, in the 20 hour digestions.

The general trend of these results is very nearly parallel with that for the total nitrogen of the digestion products.

The advantage of Method II is that it is a convenient and rapid method for the approximate measurement of proteolytic activity. Method I is upon a more sound basis theoretically and while it requires more time and manipulation it is the one that should be selected where delicacy and reliability in results are required.

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TABLE III.—ACIDITY OF CLEAVAGE PRODUCTS (VOLHARD-LÖHLEIN METHOD) FORMED BY ACTION OF DIFFERENT WEIGHTS OF COMMERCIAL ENZYME UPON 1 GM. OF CASEIN AT 40°.

	Half-hour digestions	20-hour digestions
Mg. of commercial enzyme	Trypsin I. Acidity over that of "blank," in terms of cc. 0.1 *M* NaOH	Trypsin II.
0.001	0.0	0.2
0.002	0.0	0.2
0.01	0.0	1.2
0.05	0.0	5.8
0.1	0.6	11.0
0.5	1.3	22.5
1	3.0	26.0
2	6.1	27.7
5	12.1	30.1
25	25.6	33.9
50	28.6	35.6
100	30.6	37.8

TABLE IV.—ACIDITY OF DIGESTION PRODUCTS RESULTING FROM ACTION OF 1 MG. OF COMMERCIAL ENZYME UPON 1 GM. OF CASEIN FOR DIFFERENT LENGTHS OF TIME AT 40°.

Time of digestion Hours	Acidity over that of "blank,"—cc. of 0.1 *M* NaOH	
	Trypsin I.	Trypsin II.
½	4.43	2.02
1	8.18	4.10
2	13.58	7.81
3	18.00	10.83
4	19.56	14.37
6	22.81	18.40
8	23.98	21.52
21	26.20	25.80

The temperature of 40°C. at which Sherman and Neun carried out the digestions is the optimum temperature for the action of trypsin and pepsin. Above this temperature the enzyme suffers destruction. Below 40° the activity of the enzyme is greatly retarded although it is not destroyed. The determination of the activity of the enzyme may be carried out at any temperature under 40° that the analyst may choose but the temperature must be accurately controlled and all comparisons made at the same temperature. A thermostat that does not fluctuate more than 0.1° is required in order that valid and concordant results may be obtained.

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chemistry. The author takes pleasure in making acknowledgement of Messrs. Gallun and Sons Company's support.

COLUMBIA UNIVERSITY,
NEW YORK CITY.

THE SWELLING OF LIMED AND HYDRATED HIDE IN THE PRESENCE OF ACID OR ALKALI.

By George D. McLaughlin.

Received March 18, 1920.

The phenomena of the swelling of gelatin or other protein in the presence of acid or alkali has been the subject of increasing study during the past decade. The exhaustive researches of Hofmeister,[1] Spiro,[2] Ostwald,[3] Pauli,[4] Hardy[5] and Fischer[6] have been generally used as applicable to the specific problems of the tannery chemist and yet the swelling of *hide,* as such, has received little direct study except for the work of Procter and Wilson. But even the findings of these workers are largely applications to hide of the behavior of gelatin. For these reasons the following experiments on *hide* itself seem to us of importance.

The hide used throughout our studies was in the "white" condition, just as it left the beam-house to enter the tail rocker. Our specimens were cut from "Texas" steers, of summer take-off, in healthy condition. By "healthy condition" is meant that the hide showed no signs of having experienced any untoward effect in the beam-shop process; it was plump, well hydrated and showed the average white-weight gain usual for these hides.

The specimens were cut from along the back edge of the side, between tail and shoulder, and contained 70 per cent. water. Each one gram of the *dry.* hide contained .01 gram CaO. In each of

[1] *Arch. f. exp. Path. u. Pharm.*, **27**, 395 (1890); **28**, 210 (1891).

[2] *Hofmeister's Beitrage zur. chem. Physiologie*, **5**, 276 (1904).

[3] *Pflüger's Archiv.*, **108**, 563 (1905).

[4] *Pflüger's Archiv.*, **67**, 219 (1897); **71**, 1 (1898).

[5] *Jour. Physiol.*, **24**, 288 (1899); **33**, 251 (1905); *Proc. Royal Soc.*, London, Series B, **79**, 413 (1907); *Zeitschr. f. physik. Chem.*, **33**, 385 (1900); T. B. Wood and W. B. Hardy: *Proc. Royal Soc.*, London, Series B, **81**, 38 (1908).

[6] Martin H. Fischer and Gertrude Moore: *Am. Jour. Physiol.*, **20**, 313 (1907); *Kolloid-Zeitschr.*, **5**, 197 (1909). Martin H. Fischer: *Pflüger's Archiv.*, **125**, 99 (1908); also *Oedema and Nephritis* (2nd Edition) where further experiments are detailed.

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the following experiments 30 grams hydrated hide (9 grams dry hide) were soaked for 24 hours in 250 cc. of the acid or alkali solutions. Temperatures averaged about 72° F. (22° C.). Weighings were made upon a sensitive balance after all adhering excess moisture had been removed by lightly pressing between filter paper. Equinormal solutions are employed throughout. Table I shows in per cent. of the original 30 grams hydrated hide the gain or loss in weight after immersion for 24 hours in the different acids and alkalies of the normalities indicated.

TABLE I.

Reagent	N/256	N/128	N/64	N/32	N/16	N/8	N/4	N/2	N	2/N	3/N	4/N
Lactic acid	0	2	2	8	10	18	18	15	18	20	20	22
Acetic acid	0	−2	−2	−2	0	7	10	12	13	15	20	19
Formic acid	0	−1	0	2	3	8	10	13	15	15	20	20
Citric acid	2	2	2	2	7	15	—	—	—	—	—	—
Oxalic acid	0	2	2	8	17	15	15	12	8	—	—	—
Phosphoric acid	3	3	8	13	13	15	15	17	—	—	—	—
Hydrochloric acid	0	3	13	15	18	10	5	5	−2	2	0	−12
Nitric acid	−2	2	5	7	12	8	2	2	0	0	−27	—
Sulphuric acid	0	2	2	8	12	8	7	7	3	3	3	—
Sodium hydroxide	7	8	8	7	5	5	7	10	12	27	22	—
Potassium hydroxide	8	8	7	7	8	7	10	12	17	35	42	—
Ammonium hydroxide	3	3	3	5	5	5	5	5	5	7	—	—

It will be noticed that in the case of the "weak" acids the swelling increases quite uniformly with increasing concentrations, whereas, with the "strong" acids, the swelling reaches a maximum at a certain concentration, beyond which a rapid decrease in swelling occurs. These facts are well known and have been discussed by others in previous issues of this journal. They will be referred to later.

Our next step was to determine what proportion of the weight gains shown in Table I was made up of *water* and what proportion was absorbed acid or alkali. We, therefore, determined the amount of acid or alkali remaining in the solution at the end of the 24 hour period and, after subtracting the amount of acid consumed by neutralization of the lime, calculated the rest as absorbed by the hide substance. The values found are shown in Table II.

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TABLE II.

Reagent	Concentration	Total weight gained in per cent. of original weight	Gms. weight gained per gm. *dry* hide	Gms. reagent absorbed per gm. *dry* hide excluding that used in deliming	Gms. actual *water* absorbed by 1 gm. *dry* hide	Per cent. of reagent absorbed per gm. dry hide	Absorbed H_2O in per cent.	Proportion H_2O absorbed to 1 part reagent absorbed
Ammonium hydroxide ..	N/16	5	0.1667	0.0038	0.1629	0.38	16.29	43
Potassium hydroxide....	"	8	0.2667	0.0106	0.2561	1.06	25.61	24
Sodium hydroxide	"	5	0.1667	0.0041	0.1626	0.41	16.26	40
Lactic acid	"	10	0.3333	0.0410	0.2923	4.10	29.23	7
Acetic acid	"	0	0.0000	0.0373	—0.0373	3.73	—3.73	—
Formic acid	"	3	0.1000	0.0243	0.0757	2.43	7.57	3
Oxalic acid	"	17	0.5667	0.0648	0.5019	6.48	50.19	8
Phosphoric acid.....	"	13	0.4333	0.0196	0.4137	1.96	41.37	21
Hydrochloric acid	"	18	0.6000	0.0295	0.5705	2.95	57.05	19
Nitric acid	"	12	0.4000	0.0541	0.3459	5.41	34.59	6
Sulphuric acid.....	"	12	0.4000	0.0316	0.3684	3.16	36.84	11
Potassium hydroxide....	3/N	42	1.4000	0.3733	1.0267	37.33	102.67	3
Sodium hydroxide	2/N	27	0.9000	0.1778	0.7222	17.78	72.22	4
Lactic acid	2/N	20	0.6667	0.0960	0.5707	9.60	57.07	6
Formic acid	2/N	15	0.5000	0.2663	0.2337	26.63	23.37	0.9
" "	3/N	20	0.6667	0.3543	0.3124	35.43	31.24	0.9
" "	4/N	20	0.6667	0.4182	0.2485	41.82	24.85	0.6
Acetic acid	3/N	20	0.6667	0.5374	0.1293	53.74	12.93	0.2
" "	4/N	19	0.6333	0.4307	0.2026	43.07	20.26	0.5

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TABLE III.

Reagent	Concentration	Total gms. reagent present per gm. dry hide, after deducting for $Ca(OH)_2$ neutralization	Per cent. ionized	Gms. ionized reagent present	Mols. H + or OH — present	Gms. H_2O absorbed per gm. *dry* hide
Lactic acid	N/16	0.1353	4.62	0.00625	0.0000694	0.2923
Formic acid	"	0.0691	5.89	0.00407	0.0000885	0.0757
Nitric acid	"	0.0948	100.00	0.09480	0.0015050	0.3459
Hydrochloric acid	"	0.05496	100.00	0.05496	0.0015050	0.5705
Sulphuric acid	"	0.0737	70.29	0.05180	0.0010570	0.3684
Sodium hydroxide	"	0.0694	100.00	0.06940	0.0017350	0.1626
Potassium hydroxide	"	0.0972	100.00	0.09720	0.0017350	0.2561
Ammonium hydroxide	"	0.0607	1.68	0.00102	0.0000291	0.1629
Lactic acid	2/N	4.9711	0.83	0.04126	0.0004580	0.5707
Acetic acid	3/N	4.9807	0.24	0.01190	0.0001980	0.1293
" "	4/N	6.6474	0.22	0.01460	0.0002440	0.2026
Formic acid	2/N	2.5407	0.97	0.02460	0.0005360	0.2337
" "	3/N	3.8185	0.77	0.02940	0.0006390	0.3124
" "	4/N	5.0963	0.63	0.03210	0.0006980	0.2485

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Even superficial examination of Table II indicates that—quite contrary to the general teaching—there is *no* relationship between the concentration of the hydrogen or hydroxyl ions yielded by the dissociation of these various reagents in water and the amount of swelling of hide they induce.

The comparative ionization values of the various reagents used are shown, for the concentration employed, in Table III.

If we calculate the plumping effects of these different acids or alkalies by dividing the weight of water absorbed in each case by the mols of H^+ or OH^- present, we obtain the figures shown in Table IV if the plumping effect of HCl is taken at 100.

TABLE IV.

Hydrochloric acid	N/16	100
Nitric acid	N/16	60
Sulphuric acid	N/16	92
Lactic acid	N/16	1111
Formic acid	N/16	226
Potassium hydroxide	N/16	39
Sodium hydroxide	N/16	25
Ammonium hydroxide	N/16	1477
Lactic acid	2/N	329
Acetic acid	3/N	172
Acetic acid	4/N	219
Formic acid	2/N	115
Formic acid	3/N	129
Formic acid	4/N	94

Table IV neglects the ionization value of water itself as of too small value to be of account. Also, we have figured on the basis of 250 cc. of solution without considering the 21 grams hydration water in the hide.

Table IV shows clearly that were plumping effect really determined exclusively—or even in the main—by hydrogen or hydroxyl ion concentration the ions of lactic acid, for example, would have to be assumed to be eleven times as powerful as those in hydrochloric acid; while the hydroxyl ions of ammonium hydroxide would be nearly sixty times as powerful as those of sodium hydroxide.

The theory of Procter and Wilson on the swelling of gelatin, if we understand it correctly, is as follows.

Gelatin jelly consists of a network of molecules with small interstices throughout its mass. This jelly is completely permeable to water and to the ions of acids, bases and salts which may be added, but is *not* permeable to the gelatin ion of the salt which

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is formed. When an acid is added to gelatin a salt is formed which is ionizable. The postive ion of this salt exerts an osmotic pressure on the gelatin mass, which causes the swelling to occur. The limit of swelling in any case is determined by the concentration of gelatin ions present and the natural cohesion of the jelly—the two forces opposing each other. For any particular sample of gelatin this force of cohesion is assumed to be constant, though it may vary for different samples. Hence the amount of swelling depends solely upon the concentration of the gelatin ions. The number of gelatin ions is directly dependent upon the number of H^+ or OH^- ions present. When acid is added to gelatin in increasing amounts, an increase of swelling is noted at first with all acids. With "strong" acids a maximum is reached, after which increases in acid concentration cause a decrease of swelling. With "weak" acids this point is not reached, the swelling continually increasing. The reason for this is that the swelling will increase as long as the gelatin compound is formed. After that, increase of acid will cause a decrease of swelling, because increasing concentration of the common negative ion causes a repression of ionization of the gelatin compound. With "weak" acids this point is not reached because the small ionization of such acids does not permit the gelatin salt to be completely formed. The dehydrating effect of a salt added to the acid-gelatin solution is due to the decrease in concentration of the gelatin ions, due to repression of ionization, caused by the common negative ion.

The figures in the tables above do not support such an explanation. We believe an understanding of hide swelling entails consideration of (1) the history of the hide before coming to soaks (2) the beam-house treatment. Assuming the hide to have been promptly and thoroughly salted by the packer, the changes precedent to beam-shop treatment may be assumed to have been of two types. First, those due to postmortem acid formation (mainly lactic acid) and, second, those due to the action of the salt. When the hide reaches the soaks we are not dealing with the original protein mass but with more or less of a mixture, in our opinion, containing protein lactate and sodium chloride proteinate. The amphoteric nature of the protein allows it to combine, through its carboxyl group, with any base (in this instance, the sodium of the salt) and through its amino group with any acid (like lactic or

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hydrochloric). In this state the hide is soaked and limed, whereby it is largely converted into calcium proteinate. *Each of these various protein compounds has a definite and characteristic hydration capacity.* Fischer and I have shown[1] that this is the case for soaps, which, as compounds of fatty acid (analogous to proteinic acid) with base, are identical in colloid-chemical behavior with those of the combinations of polymerized amino-fatty acids with base (which we call proteins or hide-substance).

Every tanner sees all these things before his eyes when he white-weighs regular limed stock and obtains a certain hydration figure and then treats or "plumps" the hide with an acid and obtains a new and different hydration figure.

The phenomena of hydration and dehydration as observed in the soaps are only in small measure, if at all, to be understood on any purely electrical basis, and the same is true of the swelling of hide. This is proved in the case of the soaps by observing that the same solid "gels" can be obtained whether we use water or entirely anhydrous substances like the various alcohols, carbon tetrachloride, chloroform, toluene, turpentine and benzene. In most of these non-aqueous solvents dissociation is negligible or absent.

In conclusion we would point out that the increase in weight observed with increasing concentration of acid in the case of the "weak" acids is largely explained by the absorption of acid itself (see Table II) rather than any incomplete formation of some hypothetical gelatin compound with the acid.

EICHBERG LABORATORY OF PHYSIOLOGY,
UNIVERSITY OF CINCINNATI.

THE MEASUREMENT OF THE PLUMPING POWER OF SOLUTIONS.

By Alan A. Claflin.

Received February 16, 1920.

It has long been recognized that the property of plumping, maintaining the hide as it is being tanned in a swollen condition, is an important function of a tan liquor. It has further been recognized that this property of plumping is due to the non-tanning

[1] *Jour. Lab. and Clin. Med.*, **5**, March (1920). Martin H. Fischer: *Science*, **48**, 143 (1918); *Chem. Engineer*, **27**, 155, 184, 223, 253, 276 (1919).

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acid constituent of the liquor. In consequence the determination of the non-tanning acids in the liquors has been regarded in many tanneries as a part of the chemical control work hardly less important than the determination of the tannin itself. A standard method for determining the non-tanning acids has been always included in L. T. C. procedure, although the difficulty of distinguishing between the tanning and non-tanning acids has been such that the methods chosen have only been recommended provisionally. From a scientific standpoint it has been apparent that those methods which depended upon the removal of tannin and subsequent titration of the non-tannin acid were subject to an error because all the absorbents of tannin absorb a certain and variable amount of non-tanning acid dependent on concentration, neutral salts, etc.; and those methods like the electrometric when the acid is determined in the presence of tannin err because of the acidic character of the tannin itself. Likewise, from the standpoint of tannery practice, the results obtained in terms of non-tannin acid never have seemed to consistently corroborate results observed in the yard. Two liquors having the same acid content would have noticeably different plumping properties and a liquor which in the laboratory showed less acid might have greater plumping property in the yard than a liquor which in the laboratory showed more acid.

The work of Proctor on the swelling of gels, and the well known depleting property of neutral salts indicated that plumping properties are manifestations of ionic conditions but at the concentrations which are employed in the tannery, calculations based on electrolytic data are too complex to be practically useful.

In the course of an investigation undertaken to ascertain how much lactic acid was absorbed by hide powder in different concentrations it was observed that the volume of solution filtered from the hide powder was approximately constant for a given concentration.

Solutions were made up to 200 cc. containing respectively 10 cc., 5 cc., and 2.5 cc. of 22% lactic to these were added 5 gms. of hide powder, they were uniformly shaken and allowed to stand 24 hrs., the liquor was then filtered through cotton cloth without squeezing and allowed to completely drain, the volume of filtrate measured with following results:

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	Lactic 10 cc.	Lactic 5 cc.	Lactic 2.5 cc.
1st lot	84 cc.	92 cc.	97 cc.

experiment repeated gave

2nd lot	86 cc.	94 cc.	98 cc.

A comparative experiment made with acetic acid of equivalent acidity to the 22% lactic gave the following result:

	Acetic 10 cc.	Acetic 5 cc.	Acetic 2.5 cc.
1st lot	100 cc.	109 cc.	118 cc.
Check	96 cc.	103 cc.	116 cc.

A blank experiment with hide powder and water conducted at the same time gave 194 cc. and 198 cc.

These experiments confirm the generally accepted opinion that lactic acid has a greater plumping power than acetic acid in solutions of the same concentration.

Experiments made with lactic and acetic acids, with the addition of 5 gms. of neutral salt gave the following results:
Volume of original solution 200 cc. containing 5 cc. of lactic, 5 cc. acetic to which was added 5 grs. neutral salt and 5 gms. hide powder. Volume of filtrate

Lactic cc.		Acetic cc.	
156	159	169	167

Experiments with solution containing 5 cc. of lactic and 5 cc. of acetic acids respectively and 5 gms. of dry chestnut extract 57% tannin gave the following volume of filtrate:

Lactic and chestnut exts. cc.		Acetic and chestnut exts. cc.	
110	112	116	117

Chestnut extract and water without any acid gave 127 cc. and 130 cc.

The solutions above with lactic and acetic acids, chestnut extract and 5 gms. of neutral salt, gave

Lactic, salt and chestnut ext. cc.		Acetic, salt and chestnut ext. cc.	
140	140	147	150

Further experiments were made using 200 cc. of solution containing 10 gms. of 57% chestnut extract in 200 cc. of solution containing 10 cc. of 22% lactic acid and 2.5 cc. respectively and equivalent acidimetrical quantities of acetic acid, with the following results:

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	Lactic 10 cc. vol. filtrate	Acetic 10 cc. vol. filtrate
Lot No. 1	60 cc.	80 cc.
Lot No. 2	69 cc.	82 cc.
	Lactic 2.5 cc. vol. filtrate	Acetic 2.5 cc. vol. filtrate
Lot No. 1	71 cc.	86 cc.
Lot No. 2	69 cc.	88 cc.
	Blank without acid	
Lot No. 1	92 cc.	
Lot No. 2	94 cc.	

Using same procedure except a mixture of solid quebracho extract and powdered chestnut extract totaling approximately 3% tannin to the solution of which 60% was quebracho and 40% chestnut,

	Lactic 10 cc. vol. filtrate	Acetic 10 cc. vol. filtrate
Lot No. 1	47 cc.	59 cc.
Lot No. 2	46 cc.	58 cc.
	Lactic 2.5 cc. vol. filtrate	Acetic 2.5 cc. vol. filtrate
Lot No. 1	57 cc.	80 cc.
Lot No. 2	55 cc.	82 cc.
Blank	99 cc.	96 cc.

Following same procedure using a liquid quebracho extract alone, approximately 2% of tannin in solution, and with one third of acids neutralized by lime water the following results were obtained.

	Lactic 10 cc. vol. filtrate	Acetic 10 cc. vol. filtrate
Lot No. 1	53 cc.	71 cc.
Lot No. 2	59 cc.	72 cc.
	Lactic ⅓ neutralized vol. filtrate	Acetic ⅓ neutralized vol. filtrate
Lot No. 1	76 cc.	95 cc.
Lot No. 2	75 cc.	93 cc.
Blank	109 cc.	109 cc.

The designations given as Lot No. 1 and Lot No. 2 are simply to indicate the check duplicates.

The above experiments were repeated using 10 minute mechanical shaking and filtering immediately instead of after standing 24 hours.

	Lactic vol. filtrate cc.	Acetic vol. filtrate cc.
Lot No. 1	54	71
Lot No. 2	55	73
	Lactic neutralized vol. filtrate cc.	Acetic neutralized vol. filtrate cc.
Lot No. 1	79	96
Lot No. 2	76	99
Blank	103	102

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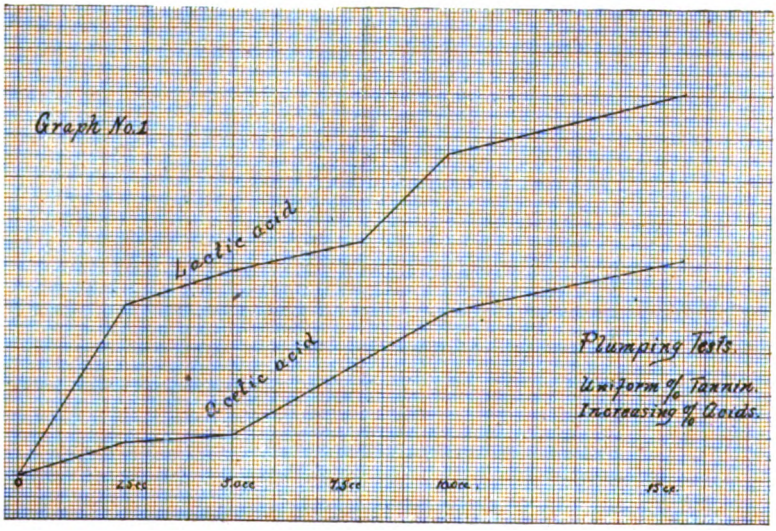
This indication that in 10 minutes of mechanical shaking the maximum of plumping is attained, is of value in enabling a quick report on plumping quality of a liquor to be obtained.

The following experiments were made filtering after shaking, and as it was desired to chart the results, they are not reported as heretofore in the volume of filtrate but in the difference between the volume of filtrate and original solution, which is the true measure of the plumping.



200 cc. of liquors were used containing approximately 2½% of tannin about one-half chestnut and one-half liquid quebracho.

	No acid	Lactic 2.5 cc.	Lactic 5 cc.	Lactic 7.5 cc.	Lactic 10 cc.	Lactic 15 cc.
A	104 cc.	120 cc.	124 cc.	126 cc.	138 cc.	144 cc.
B	105 cc.	119 cc.	123 cc.	128 cc.	138 cc.	145 cc.

	Acetic 2.5 cc.	Acetic 5 cc.	Acetic 10 cc.	Acetic 15 cc.
A	107 cc.	111 cc.	119 cc.	126 cc.
B	109 cc.	109 cc.	118 cc.	124 cc.

Graphically represented these results show curves as given in figure I:

Experiments were made using same quantity of acids, *viz* 10 cc., but using varying contents of tannin from 5/8% to 3¼%.

Acetic	3¼% Tan.	2½% Tan.	1⅞% Tan	1¼% Tan.	⅝% Tan.
A	104 cc.	118 cc.	124 cc.	128 cc.	135 cc.
B	104 cc.	116 cc.	125 cc.	127 cc.	137 cc.
Lactic					
A	124 cc.	137 cc.	140 cc.	142 cc.	158 cc.
B	125 cc.	138 cc.	141 cc.	143 cc.	157 cc.

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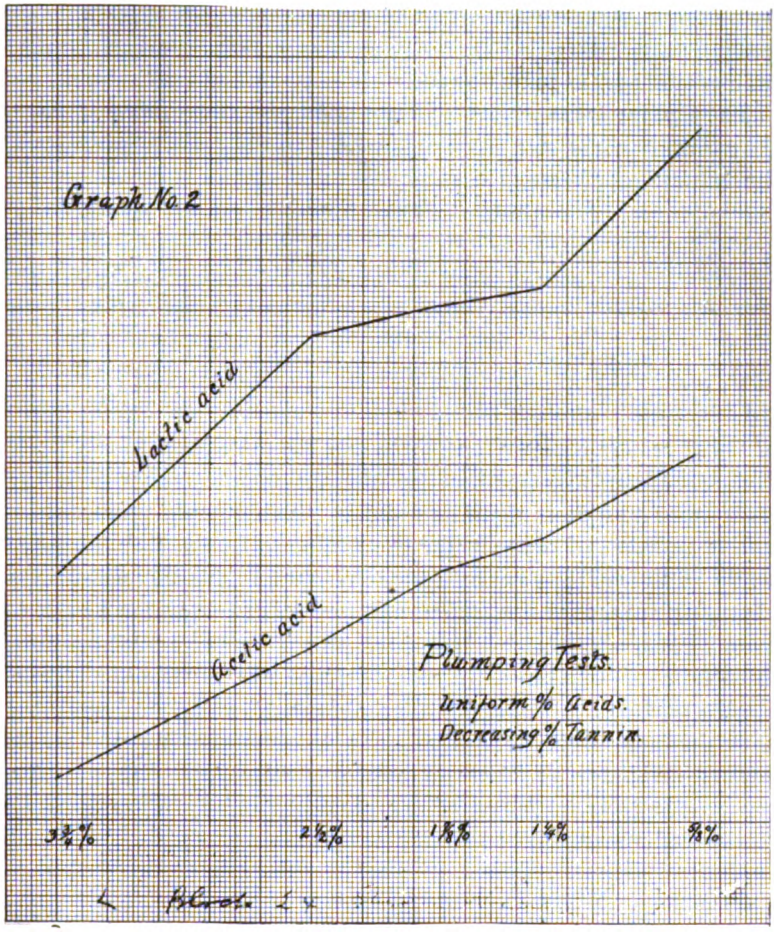
Results are reported in terms of difference or reciprocal of volume of filtrate and are shown graphically below.



Experiments made using liquors containing 1¼% tannin about ⅔ quebracho and ⅓ chestnut, and 10 cc. lactic and 20 cc. acetic, in 200 cc. gave the following results:

	Lactic 10 cc.	Acetic 20 cc.
A.....	143 cc.	136 cc. vol. absorbed by hide powder
B.....	144 cc.	135 cc.

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Experiments made using liquors made from Divi-divi, and Myrobalans. These liquors were subjected to conditions that should encourage souring, standing for 72 hrs. in warm place (100° F.) with the addition of ammonium phosphate. Comparisons are with a freshly made liquor containing about 1/3 Quebracho and 2/3 Chestnut Tannin.

The liquors were made approximately equal in tannin content, the volumes given are in cc. absorbed, that is, the reciprocal of the volume of filtrate.

Divi-divi	1.08% Tan.	.54% Tan.
A	89 cc.	93 cc.
B	86 cc.	94 cc.
Myrobalans	**1.16% Tan.**	**.58% Tan.**
A	85 cc.	87 cc.
B	86 cc.	88 cc.

Quebracho and chestnut	1.12% Tan.	1.12% Tan. and 2.5 cc. Lactic	.56% Tan.
A	76 cc.	118 cc.	84 cc.
B	78 cc.	120 cc.	86 cc.

These results indicate that some souring took place in the Divi-divi, but practically none in the Myrobalans. The addition of .25% lactic acid gave about four times the amount of plumping.

The addition of grape sugar to tan liquors is more or less generally practised in the endeavor to obtain liquors with more plumping properties. Liquors were prepared containing approximately equal amounts of Oak Bark and Chestnut extract tannin, to 1000 cc. of such liquor 30 gms. of grape sugar was added also a small amount (2 gms.) ammonium phosphate, and a similar liquor with the ammonium phosphate but without the sugar. Both liquors stood for 72 hours at approximately 100° Fahr. The results are given in terms of the reciprocal of the filtrate, using 200 cc. volume and 10 gms. hide powder.

Sugar liquor	1 1/2% Tan. cc.	1% Tan. cc.	1/2% Tan. cc.
A	89	93	96
B	92	94	94
Non sugar liquor			
A	92	93	95
B	91	92	95
Sugar liquor .25% lactic acid			
A	118	118	124
B	116	120	126
Non sugar liquor .25% lactic acid			
A	118	121	125
B	117	122	127

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The results indicate that under the conditions the sugar was without influence on the plumping.

Discussion of results: The concordance of the results obtained indicates that the measurement of the comparative volumes of filtrates on shaking with hide powder is accurate for comparative purposes. The agreement of the results obtained with what is known of the theory of plumping *e. g.* depleting action of neutral salts, and greater plumping powers of more highly ionized acids, *e. g.* lactic over acetic show the method is correct in principle. From the nature of the method and its susceptibilities to varying influences, *e. g.* the individual factor in reading volumes, observing weights, etc. atmospheric conditions and above all temperature, results are comparative only with results obtained at the same time and under identical conditions.

All the work reported has been on tan liquors prepared in the laboratory, it is hoped to continue it with the liquors occurring in the tannery.

INDUSTRIAL USES FOR THE SHARK AND PORPOISE.*

By Allen Rogers.

For several years the author has been interested in the utilisation of shark and porpoise skins for leather manufacture and has investigated the methods of handling this class of raw material. Through this work he became acquainted with Mr. Alfred Ehrenreich, President of the Ocean Leather Company, who has also spent many years in the study of this subject, and through whose efforts the establishment of an entirely new industry has been made possible.

During several recent visits to the Everglades of Florida and to Morehead City, North Carolina, the shark and porpoise have been studied in their native haunts, and the fact demonstrated beyond a doubt that it is possible to handle these animals in a commercial manner. As a result the Ocean Leather Company has now in operation at Morehead City a modern plant where the hides are removed and salted. In addition, at this plant the livers are rendered for their oil and the flesh converted into a high-grade fertilizer stock. At Sanabal Island, Florida, another factory is in the process of construction which will be a duplicate of the one at Morehead City.

* Reprinted from *J. S. C. I.* 39, 9T (1920).

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The sharks are caught in nets of 8-inch mesh, 360 yards long and about twelve feet deep, made of heavy twine. As the boat picks up the buoy, one man standing in the stern pulls in the cork line, while another hauls up the lead. When the shark is brought up a rope is placed over the tail, or in some cases, a hook is placed in the eye. If the fish is alive it is killed by a sharp blow with an axe, and then lifted on board by means of a block and fall. In an average haul from ten to twenty sharks are taken from each net.

On arriving at the dock the fish are unloaded, and the work of dressing at once started. The first operation is to remove the fins and tail. The fins are tacked on a rack and allowed to dry in the sun; they are used by the Chinese for making soup. The fish is then cut down the back, and a circular cut made over the neck and around the gills. The skin is finally removed in such a manner that only the hole of the pectoral fins and rectal opening remain in the pelt. The flayed skins are placed in salt for 24 hours, fleshed on the beam or machine, and then pickled with salt and sulphuric acid. The pickled skins are drained and placed in bunbles for shipment.

The livers are thrown into barrels, where they are allowed to remain for several days to disintegrate, and then placed in steam-jacketed kettles and heated to boiling for about one hour. From the kettles the oil is run into washing and settling tanks, where the gurry is separated from the oil. The oil is then drawn into a second tank, again washed, and finally run to a third tank, where it is stored until ready for shipment. Exposure to the sun and rain effects more or less bleaching.

The carcase of the shark may have possibilities as a food product, but at present is being used in the manufacture of fish scrap for fertilizer stock. The carcase is thrown into the hopper of a specially-designed mill, where the flesh and bones are ground to a fine pulp, which is dried in a rotary dryer. This grade of fish scrap contains on an average 15—17% of nitrogen expressed as ammonia.

The shark skins as they arrive at the tannery at Newark, N. J., are soaked in water to remove the salt and again fleshed. The skins for bag leather are limed and bated in the usual manner and tanned in bark. The tanned skins are then treated with strong hydrochloric acid by the Kohler process to remove the

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shagreen, and after washing and colouring are ready for the finishing process.

The skins to be used for shoe leather are not limed or bated, but are at once treated for the removal of the shagreen. This so-called shagreen is a very hard layer which covers the whole fish; it has the appearance of very coarse sand paper and is almost impossible to remove by mechanical means. The elimination of shagreen from the raw skins is a problem which until recently has remained unsolved. A process discovered by the author which consists in soaking the skins in a salt solution of 10° B. (sp. gr. 1.074) mixed with an equal volume of hydrochloric acid. The removal of the shagreen is accomplished in about two hours. By leaving skins in this solution for a week no damage occurs. The skins are neutralized in a salt solution of 10° B., to which soda ash is added from time to time. When free from acid the stock can be tanned by any of the methods now in vogue.

For several years the Bureau of Fisheries has endeavored to interest the public in using shark meat for edible purposes with a certain amount of success. In fact, that species of shark known as dogfish is being canned in large quantities and sold under the name of grayfish. Some of the larger sharks are sold in certain markets as deep sea sword fish. In some places shark meat as such is offered to the trade and finds a ready market. When popoular prejudice has been overcome it must be admitted that shark flesh is a fair rival of the halibut, better than the cod, and equal even to the much-prized sword fish.

The Ocean Leather Company alone expect to bring their catch to 1000 sharks per day, and with an estimated catch by other fishermen of 1000 daily we would have 2000 sharks averaging 100 lb., representing a supply of edible material to the amount of 75,000,000 lb. annually. If it should prove impossible to get this material to the market in a fresh condition, it is easily cured with salt and borax, and then compares favourably with any good grade of salted fish. It may also be smoked or kippered.

During numerous trips to North Carolina and to Florida a vast amount of data has been accumulated which is of value in determining yields and cost of production. Included in these data are many individual records, some of which may be of interest as

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showing the size of fish and products secured. They are as follows:—

	Length		Girth		Weight	Weight of liver	Size of skins
	ft.	ins.	ft.	ins.	lbs.	lbs.	sq. ft.
Tiger shark, male.....	7	8	3	0	128	24	9
" " female*....	15	4	6	8	—	—	28
Cub shark, male	10	6	4	8	337	82	14
" " female.....	11	6	5	2	360	33	18
Sand shark, female.....	8	2	3	8	271	28	10
Hammerhead shark, male	5	8	2	3	56	6	4

*Oil rendered, 21 gallons.

It will be seen that the ratio of liver to body varies in the different species, and also that in the same species there is a difference between male and female.

Although the porpoise are not so plentiful as sharks they deserve brief mention. Porpoise travel almost exclusively in schools, and are, therefore, usually caught in the purse seine. The method consists in surrounding the school and then landing them on the beach. These fish vary in size from 3 to 30 ft. Their skin carries a heavy layer of blubber, which is split off and rendered to obtain lubricating oil. On the face of the fish is an extra heavy blubber known as junk, which, when rendered separately, yields a more valuable oil than ordinary blubber oil. In the jaw cavity is a small amount of oil, about 1 oz. to a fish, known as jaw oil. This oil is carefully rendered and brings from $30.00 to $80.00 per gallon.

The flesh of the porpoise is very dark in colour and resembles liver in flavour. When cooked like beef it is very tender and delicious. The same prejudice is held for porpoise as for shark, so time must be allowed for the public to become educated to this food material. In the meantime the body is utilized for making fertilizers.

ABSTRACTS.

Structure of Gelatine Solutions. By F. C. THOMPSON, *J. S. L. T. C.* 3, 209 (1919). The theory of structure for gelatin solutions supported is that such solutions consist of a network of solid gelatin, molecular, or

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at least extremely fine, with pure water in the interstices. This view differs from that of Bütschli, which assumes a network with mesh coarse enough to be observed microscopically. Gelatin solutions of greater strength than 0.18 per cent. are to be regarded as elastic solids, although too dilute to set to jellies. This is because they will resist a small shearing force indefinitely. The solutions most probably have a network structure formed of solid gelatin, with pure water in the interstices. This structure gives a high apparent viscosity to the solution as measured by direct methods such as flow through a capillary tube, because of the resistance to rupture offered by the network. Diffusion and conductivity experiments show that electrolytes in gelatine solutions behave as though dissolved in a medium of viscosity equal to that of water, *i.e.*, in water itself. Ions appear to move in the water of the interstices, and are only slightly obstructed by the solid network in solutions up to 2-3 per cent. strength, though here the apparent viscosity of the solution is high. Quincke's two-phase theory explains many of the facts, but not all. The vapour pressure of even stiff gelatin jellies is practically identical with that of water, thus indicating the presence of pure water.

Sugars in Mimosa Bark and Extracts. By A. HARVEY, *J. S. L. T. C.* 4, 11 (1919). Sugars, both mono- and di-saccharoses, are present in considerable quantities in unadulterated Natal mimosa barks, and in extracts prepared therefrom. The total amount of sugar in extracts appears to increase with increasing extraction pressure. Probably hydrolysis of cane-sugar or other di-saccharoses to glucose or other reducing monosaccharoses takes place in the manufacture of extracts, especially when high pressures are used.

Note on the Detection of Sulphite-Cellulose in Tanning Extracts. By G. F. KNOWLES, *J. S. L. T. C.* 4, 13 (1919). A modified form of the Procter-Hirst test, in which formic acid is substituted for hydrochloric acid does not give a precipitate with sulphited pure quebracho extracts, as does the original test. Nevertheless a positive test with the modified procedure does not necessarily indicate sulphite-cellulose, as synthetic tannins give a precipitate.

Note on the Analysis of Lime Liquors. By F. C. THOMPSON and W. R. ATKIN, *J. S. L. T. C.* 4, 15, (1919). The precipitates obtained by neutralising lime liquors with acids and by the so called "tanners' test" have been shown to be due entirely to dissolved epidermal matters and not to true hide substance at all. These precipitates are not given by solutions obtained by treating pure gelatine or hide powder with solutions of lime or of lime and sodium sulphide.

Leather in the British Engineering Trades. By F. R. PARSONS, *S. & L. Rep.*, Feb. 26, 1920, 83. No use to which leather can be put provides a greater test for quality and durability than does its employment in hydraulic and pump installations. The very best and most carefully

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selected hides are not a bit too good for this form of service. And the best is cheapest—always.

Pump valves, clacks, and barrel sweeps call for the services of a type of leather that shall combine the qualities of durability and a maintenance of soft, pliable conditions. This is ensured only if the leather is taken from the best portions of the butts, and properly oil-dressed. Cup leathers in particular call for the best of material. But in this connection it may not always be the material that is at fault when, as not infrequently happens, a cup leather will seem to wear out in a very short period of time.

This is often due to the fact that the cup has been pressed to shape with the skin side outwards. In the writer's opinion this is a mistake. Cup leathers pressed with the flesh side outwards not only wear much longer, but make a more perfect watertight joint; its longer life being largely due to the fact that the outer and stronger fibres of the leather make a better wear resister. Indeed, common sense would seem to suggest that as soon as the skin is worn or cut through the fibres would as a consequence become so much weakened as to quickly give out under further strain or wear. At any rate, this is an engineer's assumption, open to correction if wrong.

Then, again, it may often occur that the material is condemned as of inferior quality, because it has never received fair service treatment. We remove from a pump, say, a cup or a valve, and find them hard and brittle, breaking away in the fingers under slight pressure. Poor quality material? Not necessarily. More likely it is due to a lack of nourishment. Always should a cup leather or a valve clack, or a barrel sweep be well soaked in hot tallow before being put into service, then the tallow well worked into the leather with the hands.

Another way of conditioning leather for cold water service is to soak it in neatsfoot, sperm, olive, or castor oil. But in no case be ever guilty of using mineral oil, or even lubricating oil; these will inevitably tend to make the leather rotten and pulpy. A pump leather that through neglect has become hard and brittle may be partially recovered by soaking it for a while in warm water—not hot—then when dried off again soaked in warm tallow or any of the oils mentioned.

Although leather hose is not in so great a demand now as formerly, having been largely superseded by woven textile material, there are still many occasions, notably in dredger work, where leather is found to be the most efficient as well as the most durable of material.

The efficiency and durability of leather hose depends to a great extent upon the care and attention bestowed upon it when both in and out of service, for it might take more harm when lying idle than when at work. If used in salt water, as it often is for harbor purposes, it will naturally require considerably more nourishment than that used in fresh water, as the salt acts upon the properties that constitutes its pliability.

To re-condition either leather hose or leather fire buckets they should be well washed and brushed with fresh luke-warm water, afterwards

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applying by hand a good dubbing, or otherwise a mixture of tallow and cod oil rubbed in warm with a stiff brush, when the leather is in a semi-dry state.

In leather the engineering trades possess a material that is recognisedly without a rival, nothing so efficiently takes its place, nothing can be cited that is "just as good." But what in every case is demanded of it is that it shall be of the very best material. In engineering service leather is put upon its merits, it is called upon to perform functions the like of which are not shared by any other material under the sun, its duties are more often than not arduous and exacting. It is often terribly abused.

But despite all this if we start with the best possible conditions of service in the way of material, if we fully recognize that good qualities are inherent only as long as they are artificially maintained, then shall we, as engineers, have little cause to go farther afield in search for a more satisfactory, a more durable and efficient substitute.

The Analysis of Sole Leather; the Determination of Water-Soluble Matter by the French and English Methods. M. JALADE. *Le Cuir* VIII, 394-7 (1919). In commenting upon the organization of the Committee on the Analysis of Vegetable-Tanned Sole Leather of the Society of Leather Trades' Chemists, Jalade expresses doubt as to the effectiveness of committee work, arguing that the defect inherent in such committees lies in lack of intimacy and proper contact of the several members; each isolated in his own sphere and occupied with daily routine is not generally disposed to give the time required to solve the problems confronting the committee. It would be more profitable to encourage all chemists, whether members of the Society or not, to make known their findings in regard to any analytic work whatsoever, the same to be given as wide publicity as possible among those interested. This would cause lively discussion through the technical journals which should steadily increase in interest and which might prove useful even to the tanners themselves, tempting them to voice their own opinions.

The specifications for leather supplies required during the war by the French Commissariat, which include methods of sampling and analysis, were drawn up by Messrs. Balland, Meunier, and Jalade and were accepted without comment by the French General Syndicate for Hides and Leather. Jalade considers the methods given in these specifications as completely satisfactory and he objects to Dr. Parker's intention to work to produce methods capable of giving more exact results as an exaggeration hardly likely to advance the question of leather analysis, since small errors make but little difference in the matter of judging leather, especially since the leather is not homogeneous. What is really essential to form sound conclusions is the general trend of the analysis and the relation of the various determinations to one another. Of very great importance also in passing judgment on leather are the odor, taste, color, resistance to cutting, compactness of the fibers, color of the cross section, and, in fact, all its physical properties.

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What is really desired is the establishment of uniform methods. In the *Journal of the Society of Leather Trades' Chemists* for February, 1918, we find a method for the analysis of sole leather differing in many respects from the French method. These differences should be studied so that one method for all might be evolved.

One notable difference lies in the determination of matter soluble in water. The French method is as follows: The sample is cut with a plane, giving pieces less than 0.5 mm. thick. Care must be taken that the sample for this determination is never heated. Five grams are degreased by leaching with petroleum ether in the cold and then exposed to air until all solvent has evaporated, which takes from 4 to 5 hours. The sample is then put into a flask with 250 cc. water at 15° and shaken in a mechanical agitator for 5 hours, after which it is allowed to stand for 1 hour. It is then filtered, using a Berkefeld candle connected with a vacuum pump; or it may be filtered through a good paper, provided the first 50 cc. of filtrate are rejected. Of the clear filtrate 50 cc. are evaporated, first on a water-bath and then to constant weight in an oven at 100°. The residue is taken as the water-soluble matter in 1 gram of leather.

By the English method, the sample is first finely divided with a spoke-shave and then ground in a mill or cutting machine. A 25-gram sample is freed from grease by extracting for 6 hours in a Soxhlet apparatus with petroleum ether boiling between 40° and 60°. The leather is then spread on a plate and left in a warm place until the solvent has evaporated. It is then put into a Procter extractor, without any sand, covered with water and allowed to stand over night. Next day the extractor is heated to 45° and the sample extracted at such a rate as to give 1 liter of extract in 3 hours. The extract is filtered through good paper, the first 200 cc. being rejected. 50 cc. of the clear filtrate are evaporated to dryness on the water-bath and dried in a vacuum oven for 2 hours.

The two methods were compared, but with the following changes: The leather was simply planed according to the French method and was not ground after this. 20-gram samples were degreased in a Soxhlet apparatus with petroleum ether boiling at 65°. The extraction was made in a Jalade extractor (cf. This JOURNAL, XIV, 703 (1919) instead of the Procter extractor. These slight changes in detail in the English method should not influence the final results appreciably. Two sole leathers of French manufacture and one of American origin were analyzed and the results are given in Table I.

It should be noted that the English method gives much higher results than the French method, a fact which merits the attention of the special Committee of the S. L. T. C. and should interest the tanners, who ought to specify the method employed in order to avoid dispute where analyses of their leathers are required.

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TABLE I.

	French Butts				American Butt	
	Smooth		Rough			
	Water solubles		Water solubles		Water solubles	
	Per ct. of original leather	Per ct. of dry and degreased leather	Per ct. of original leather	Per ct. of dry and degreased leather	Per ct. of original leather	Per ct. of dry and degreased leather
French Method.. ...	9.40	11.20	10.10	12.50	22.50	28.10
English Method.....	13.00	15.50	13.45	16.40	29.05*	36.30

* When this leather was not previously degreased, the value 28.10 was obtained. The leather contained 5.20 per cent. grease.

J. A. W.

Synthetic Tannins. GEORGES VIÉ. *Le Cuir* VIII, 424-6 (1919). Although chrome tannage may prove of greatest importance in replacing vegetable tannage, when the natural tannins become scarce, recourse will certainly be had to synthetic products resembling the tannins. The discovery that water-soluble tanning materials can be produced by the action of formaldehyde upon phenolic compounds solved the question of cost in the manufacture of such products. This action has given rise to many interesting experiments, but most of the products of reaction are insoluble in water. The reaction products of formaldehyde and phenols in neutral or alkaline solution have no tanning properties, but when the reaction is carried out in acid solution in such a manner that only water-soluble products are formed, these products resemble vegetable tannins in many physical and chemical properties, but especially in tanning power. The operation is conducted in three steps; preparing the tanning product; rendering it soluble; and neutralizing the final solution.

The synthetic tannin Neradol may be prepared by mixing the following:

Phenol	80 parts
Sulfuric acid (66 Bé)	50 parts
Formaldehyde	30 parts
Water	200 parts

Care must be taken to cool the solution while mixing, for otherwise there will be formed a viscous product impossible to render soluble later. This mixture is kept at a temperature of 85° for about 10 or 15 minutes. until an oily product is obtained of such consistency that it can be separated by decantation after cooling. The product is then rendered soluble by sulfonation, which is done by heating the above mixture to 110° with 60 parts of sulfuric acid for 5 or 6 hours, or longer if the product is not rendered soluble in this time. Samples are tested from time to time for solubility; when the product is completely soluble, it is cooled, dissolved in a minimum quantity of water, and neutralized with sodium car-

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TABLE I.

Experiment No.	Proportions employed				Temp.	Degrees Bé of product	Analysis of product calculated to 25° Bé		Tintometer	
	phenol	water	sulfuric acid (66° Bé)	form-aldehyde			Tannin	Non-tannin	red	yellow
1	100	200	50	25	100°	22.7	30.2	16.0	0.1	0.5
2	80	200	50	30	130°	30.0	20.5	17.7	0.5	0.8
3	80	200	50	30	60°	22.3	30.0	9.4	0.5	0.8
4	80	200	50	30	150°	17.0	21.3	17.6	1.9	2.1
5	80	200	50	30	80°	27.0	21.8	25.8	0.6	0.5
6	80	200	50	30	160°	21.9	11.0	23.0	0.3	0.7
7	80	200	50	30	120°	27.6	24.2	18.5	0.5	0.5
7A	80	200	50	30	120°	24.4	22.2	21.8	3.2	9.1

TABLE II.

Experiment No.	Proportions employed				Temp.	Degrees Bé.	Tannin	Color of tannage
	phenol	water	sulfuric acid	formaldehyde				
10	100	200	40	25	100°	23.3	39.9	rose red
11	80	200	50	25	100°	33.0	47.7	deep violet red
12	80	200	100	30	100°	—	—	light rose
13	60	200	100	30	100°	25.8	30.0	light rose
14	60	200	100	30	95°	29.1	27.5	light rose
15	100	200	50	30	95°	33.3	24.0	rose
16	100	200	50	30	125°	30.0	24.0	pale rose
17	100	200	50	30	60°	22.3	26.9	nearly white
18	200	200	100	40	100°	—	22.0	rose
19	200	200	100	40	125°	—	10.4	rose red

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bonate. Neradol is readily soluble in water, is semi-colloidal (as can be shown by dialysis), gives a deep blue color with iron salts, gives precipitates with solutions of gelatin, lead salts, and aniline hydrochloride, will tan hide and can be used in conjunction with other tanning materials.

In Tables I and II are given the results of experiments dealing with the preparation of synthetic tannin according to Austrian patent 58,405. In each case the tannin content has been calculated to the basis of a density of 25° Bé. These experiments indicate how to prepare a product containing on an average 30 to 35% of tanning material, the same as ordinarily furnished by those firms manufacturing it. The hide-powder method is not well adapted to the analysis of Neradol, it being difficult to get concordant results with the same sample, which explains the discrepancies shown in the table.

In order to produce a leather of good quality less Neradol than vegetable tanning material is required, which shows that the synthetic product has the greater tanning power.

Neradol is almost the only synthetic tannin of practical importance. It gives a nearly white leather, surpassing sumac extract in this respect. The fibers of Neradol leathers are long and compact, but lack plumpness, which makes it valuable rather for light skins, such as those of the sheep and goat, and such leathers have considerable commercial value on account of their whiteness, flexibility, and great strength.

Another point of interest is that by using Neradol in conjunction with other materials a leather of brighter color is obtained. When used in the final liquors, it acts as a bleaching agent. Remarkable results can be obtained with strap and belting leathers by treating them with Neradol after they have been drawn from the final liquors; the yield is appreciably increased, the color brightened, and the loose tannins fixed upon the fibers. And finally it should be pointed out that leathers treated with Neradol absorb fatty matters more readily than otherwise.

The probable future of Neradol lies in its use in combination with quebracho, mangrove, or those materials which are not now used in the tannery on account of the undesirable color which they give to the leather. J. A. W.

Logwood Extracts. GEORGES VIÉ. *Le Cuir* IX, 50-2 (1920). While logwood is used for coloring, it is worth knowing that it is also an excellent tanning material, giving a leather quite the equal of those obtained by the ordinary vegetable tannage. Where a leather is later to be colored with logwood, it is advantageous to mix the logwood with the other extracts during the tannage. This makes the coloring process take less time and results in a more uniform color. For blacks, logwood may be added to the other tanning materials to the extent of from 10 to 15%.

Two good samples of logwood from Jamaica showed by the I. A. L. T. C. method:

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	Per cent.	Per cent.
Water	17.50	19.39
Total solid residue	15.06	15.25
Soluble matter	13.51	13.70
Insoluble matter	1.55	1.55
Tannin	6.92 (?)	7.11 (?)
Non-tannin	5.03 (?)	5.60 (?)

Three different samples of logwood extract showed:

	Per cent.	Per cent.	Per cent.
Insoluble matter	0.25	0.19	0.23
Soluble matter	44.52	39.97	41.67
Tannin	23.70	20.84	21.32
Non-tannin	20.82	19.13	20.35

In extracting logwood upon a commercial scale, the use of autoclaves is becoming general. The oxidizing agents at present in use are sodium nitrite, lime water, sodium carbonate, potassium ferrocyanide, and potassium permanganate; only a few tenths of 1% on the weight of the wood are used. J. A. W.

Chrome Tanning. LOUIS HOUBEN. *Le Cuir* IX, 41-2 (1920). Reckoned on a chromic oxide basis, sodium bichromate is very much cheaper than chrome alum, but yet many tanners continue to buy the more expensive material. It might at first seem that these tanners had fallen into a rut and were ignoring the benefits of modern science, but a much deeper reason for their apparent aversion to bichromate is to be found in the manifold properties of chromium compounds. Although these curious substances have been extensively studied, their behavior under different conditions is still but imperfectly understood. Chromic chloride is capable of undergoing such change that some of its chloride atoms are no longer precipitable from solution by silver nitrate, while it is possible so to alter chromic sulfate that as many as two of its sulfate groups cannot be precipitated by barium chloride. A solution of chromic sulfate made basic by adding sodium carbonate behaves very differently from one of apparently the same composition made by adding the calculated amount of sulfuric acid to chromic hydroxide. The resistance of a chrome liquor to precipitation is increased by adding potassium sulfate. The properties of chrom liquors are also altered by organic matter, and even by mere aging. When we consider that the tannage is materially affected by these changes of properties, it is easy to see why a tanner should hesitate to change his process for something cheaper, especially when he is using a substance, like chrome alum, of definite crystalline structure and therefore of fixed properties.

The author describes some attempts to use chrome liquors made by reducing bichromate. A bath made by mixing 6 molecules of HCl, 1 of H_2SO_4, and 3 of $Na_2S_2O_3$ to 1 $K_2Cr_2O_7$ readily tanned his stock, but produced a badly marbled grain regardless of the precautions taken to

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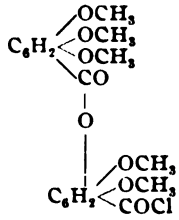
regulate the concentration of the liquors. On the other hand, a liquor made from 6 kg. of sodium bichromate, 3.25 kg. of sulfuric acid, and 1.5 kg. of glucose gave results identical with those obtained with chrome alum. J. A. W.

Vegetable Tanning; Chemical and Theoretical Considerations. C. SCHIAPARELLI. *La Conceria,* Sept. 30, 1919, through *Le Cuir* IX, 38-40 (1920). By the action of diazomethane upon tannin, Herzig prepared methyl-tannin, which gave upon hydrolysis trimethylgallic acid and asymetric m. p. dimethylgallic acid, showing that digallic acid results from the union of two molecules of gallic acid by condensation of an OH- with a COOH-group.

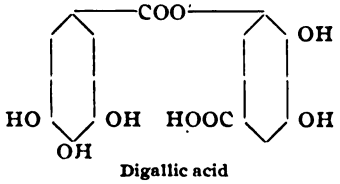
Fischer and Freudenberg prepared the crystalline compound



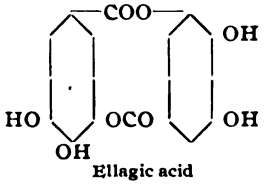
and by combining it with glucose obtained pentamethyl-m-digalloyl-glucose which strongly resembles the methyl-tannin obtained by Herzig from the natural product. This is where progress in the synthesis of tannin stopped at the outbreak of the war.

But the foregoing pertains only to gallotannic acid, or the tannin of nutgalls. By hydrolysis, the chebulinic acid of myrobalans yields some glucose, but the tannin of hamamelis gives a new sugar. Nevertheless most tannins seem to be esters of phenolcarbonic acids and glucose, or glucosides.

The work on the synthesis of the tannins has not given any basis for a new classification of them. The most satisfactory system is still that of separating them into the two groups, pyrogallol and catechol; the former yield ellagic acid and the latter phlobaphenes. To these substances are attributed the resistance of sole leather to water. According to Nierenstein, ellagic acid is formed from digallic acid.



Digallic acid



Ellagic acid

In the development of theories of vegetable tanning, our meagre knowledge of the chemical composition of the tannins has not been of great assistance. Investigations are made difficult by the fact that tanning

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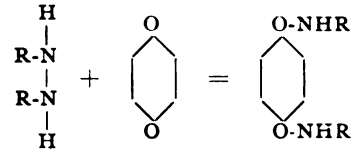
materials are mixtures of very complex substances of high molecular weight and non-crystalline form, which are not easily purified. Three types of theories have been advanced, namely, the chemical, by combination; the physical, by adsorption; and the physico-chemical theory, which appeals to the author as the most probable.

Fahrion's view of the tanning process is that it consists of two operations, the oxidation of the hide substance and the subsequent combination of this oxidized protein with the constituents of the tan liquor having quinone groups. The oxidation of the hide substance is represented by the equation

$$2(R\text{-}NH_2) + O = H_2O + R\text{-}\overset{H}{\underset{|}{N}}\text{-}\overset{H}{\underset{|}{N}}\text{-}R$$

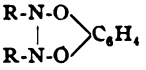
and the final transformation into leather by



hide substance quinone leather

According to this view only those tannins which are oxidized can produce leather and consequently the tanning action is greater where access to air is greater; for example, the action would be much greater in a drum than in a pit.

Meunier and Seyewetz see in the tanning process two very distinct phenomena: simple absorption of tannin and the action of rendering the hide fiber insoluble. The tannins diffuse into the hide substance and then the hide substance becomes oxidized by the peroxide groups of some of the tannins giving a protein represented by the formula R-N = N-R, which in turn combines with the quinone groups of the tannins to make leather,



Part of the oxidized tannins are reduced by giving up their oxygen to the hide substance and the remainder combine with the oxidized hide. The reduced tannins have lost their tanning properties and are very abundant in spent liquors. Only the oxidized tannins can tan and Bofinger attributes tanning properties only to such materials as are capable of furnishing phlobaphenes.

The tannin of nutgalls studied by Fischer contains no oxidation products, nor phlobaphenes, and does not produce a true leather. J. A. W.

Progress in Tanning in the Year 1918. By R. LAUFFMANN. *Gerber* 45, 45 et seq. (1919). (NOTE.—References to and extracts from literature in this JOURNAL has been purposely omitted.—*Translator.*) During the last

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year of the war the leather industry had to contend with technical and economic obstacles in increased numbers, which played an important rôle by bringing to attention, works relating to the progress of the substitution of raw and auxiliary materials as well as leather. L. Bum[1] reported on the leather division of the Substitute Show which occurred in Vienna; L. Pollack[2] on the obstacles originating in the coal and tanning material deficiency in the Austrian leather industry and the substitution of vegetable by artificial tanning material, especially Neradol. R. Lauffmann[3] in the "German Leather Industry During the War" showed that the leather industry had shown growth in spite of all the obstacles and gave the means which had made this possible. Another treatise by L. Pollack[4] described the prospective relations and prospects of the leather industry after the war and considered especially the value of raw material and tanning material, wages and cost of production and leather values. There is also a treatise by C. Schieffkorn[5] on the organization of leather trade workers and another by F. Kohl[6] on some necessary improvements to be started in the leather industry.

The Hide.

In a treatise on the molecular structure of leather[7] W. Möller summarizes his view on the structure and behavior of the smallest units of the fibrous connective tissue (fibrils) of the hide as follows: The fibril of the connective tissue is an elastic, flexible, soft crystal of thread-like nature and of ultra microscopic fineness. The individual fibrils are united in the hide fiber to form complexes, and the spaces between are filled with an inter-fibrillar substance, which is not capable of forming fibrils. The fibrillar complexes slide and move easily against one another. The fibrils move within the complexes more or less, according to the method of tanning, but not, on the whole, like the complexes themselves. The fibrils consist of micellar rows after the manner of Nagel's filaments and the individual micells can change their position with relation to one another in the micellar union owing to mechanical, chemical or other influences. The micell possesses a kind of polarity in two directions, which cannot be changed, mechanical action merely leads to a displacement of the micells toward each other. The same author in a treatise "On the Biological and Chemical History of the Hide and Pelt,"[8] on the basis of the results of earlier investigations and his own research on the elastins, their relation to the tanning process and the formation of leather, arrives at the following principle results: The content of elastic fibers in the hide

[1] *Gerber*, 1918, 201.
[2] *Allgemeine Gerberzeitung*, 1918, Nos. 27 and 28.
[3] *Gerber*, 1918, 281.
[4] *Gerber*, 1918, 61.
[5] *Gerber*, 1918, 89.
[6] *Gerber*, 1918, 266.
[7] *Collegium*, 1918, 137. Abst. this JOURNAL 14, 124 (1919).
[8] *Collegium*, 1918, 105.

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depends on the age and the mode of feeding the animals, the amount existing in the hide on account of the former is considerable. In general it is assumed that the elastic fibers result from the collagen fibers. The substance of the elastic fibers, elastine, is entirely distinguished from collagen by its composition and properties. Elastin purified by the acetic acid method, according to Schwarz has the following composition:—C—53.95, H—7.03, N—16.67, S—0.38. These figures deviate from those found by Von Schroeder for hide substance from all parts. In the cleavage products of elastin is found an essentially larger amount of glycocol, alanine, phenylaline and above all, lencine, besides tyrosine which is not formed from collagen. On the other hand a large amount of glutamic acid is formed from collagen against a very little from elastin. The elastic fiber is generally more resistant than the collagen fiber. Against boiling water the elastic fiber, in contrast to the collagen fiber, is very resistant and shows in this respect, and also with relation to its elastic qualities and refractivity, similarity to fibers from chamois leather. The tanning of the elastic fiber is probably effected by fat or protein containing materials. Elastin is dissolved by trypsin, pepsin and certain bacterial enzymes, while collagen is very resistant to these. Owing to its resistance to alkalies, elastin is preserved as such on liming but on bating a complete solution and removal of elastin occurs, which brings about a far reaching structural change of the hide.

The presence or otherwise of elastic fibers in the unhaired hide is of the greatest importance for leather making and for the kind of leather to be produced. A bated hide, that has had all of the elastin removed, cannot be made into serviceable sole leather because the deficiency resulting from solution of the elastin can never again be filled, so that a sufficiently solid structure will be obtained. On the other hand, elastin should not exist in too large a quantity because the elastic fiber does not take up as much tannin as the collagen fiber, which would influence the gain and firmness of the leather. In hides for upper leather, too great a content of elastic fibers acts unfavorably because after the removal of the elastin by bating, too many interstices and voids exist whereby a loose leather with inferior yield will be obtained.

Paessler and Sluyter[9] have exhaustively investigated the composition of raw kips and other dry foreign hides. The water content varies between 13.0 and 20.1%. There is a fairly great variation in ash content even for the same kind of hide. The lowest ash content amounted to 1%, the highest 8.7%. The natural ash content of dried hides should rarely go over 2%. Higher ash content was given by a kind of North Western hides (dry salted), Dacca kips, which includes the coated kips, a kind of China hides and Sallavery hides. The mineral matter in the dry salted North-Western kips consists mainly of sodium sulphate, magnesium sulphate and common salt and small quantities of earthy matter and gypsum. The coating of the coated kips consists largely of sodium sulphate, and contains besides smaller, yet considerable quantities of mag-

[9] *Ledertechn. Ruud.*, 1918, 17.

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nesium sulphate, potassium sulphate, earthy matter and common salt. The mineral matter of the China hides consists largely of earthy matter, common salt and small quantities of gypsum. The mineral matter of the Sallavery hides consists principally of common salt besides small quantities of sodium sulphate, potassium sulphate and earthy matter. Of the other foreign hides, the transparent China hides show the lowest content of mineral matter (1.0 to 1.5%). Higher content of mineral matter was found in the Dakar hides, Dar-es-Salam and Mombasa, the highest (6.1%) in the Abyssinian and Gold Coast hides. The mineral matter in the majority of these hides consists predominantly of common salt, the remainder consisting of small quantities of calcium sulphate, silicic acid and iron and aluminum oxides. The fat content of dried hides is mostly low. The natural fat content of properly fleshed hdes is low with few exceptions. Higher fat content is explained either by the hides being naturally richer in fat, badly fleshed, or artificially weighted by rubbing in fat. In this examination the fat content was found to be largely between 0.5 and 2.0%. Values exceeding 2.0% were found in a hide from North-Western kips (5.2%), in two Agra kips (7.1 and 9.6%), a Mombasa hide (4.1%), two hides from the Gold Coast (4.1 and 6.3%), and above all, in three China hides (13.2, 20.3 and 21.1%). In the latter more fat was contained in the firmer parts of the hide than in the neck.

Preparation of the Hide for Tanning.

A new process by G. Pollak (Ger. Pat. 304,973) for soaking and liming hides with actual agitation of the lime liquors is characterized by using a common stirring space for all of the liming vats. From this common vat the liquor is raised into the liming vats so that it flows back again naturally. The advantages quoted are: the complete washing of the hides with the liquor; prevention of the formation of sediment in the liming vats, rational utilization of the lime liquor and economy of labor. According to this process the hides remain fixed from beginning to end of the process and there is a subsequent shortening of the soaking and liming process on account of the advantages mentioned.

A. Matthesius[10] carried out practical experiments with the "ara-liming" of O. Röhn and reported very favorable results with many advantages. V. Mikuschka[11] also reported good results by the use of this process for the manufacture of washable glove kid leather, and in contrast to the excrement bate always obtained a leather of pure white color.

In a procedure for deliming and bating by E. Luksch (Ger. Pat. 305,808) the spent liquor obtained from the various processes of producing tartaric acid from crude tartar is used, concentrating the liquor if necessary. An especially favorable bating action is obtained which can be traced directly to enzymes contained in the spent liquor. The liquor sium chlorides, which act as preservative on the hide and small quantities also contains pentosans which accelerate the deliming, calcium and potas-

[10] *Ledertechn. Ruud.*, 1918, 57.

[11] *Gerber*, 1918, 63.

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of tartrate salts, which will have a favorable influence on the tanning.

M. Zsuffa[12] describes a procedure for the determination of the pelt weight and for the control of the entrance weight of raw hides, which depends upon the drained pelts being weighed under water and calculating the weight of hide substance by the formula $H = \frac{W - S}{S - 1}$, where W is equal to the water weight and S, the specific gravity of the hide substance. The weight of hide substance can be obtained on limed pelts by multiplying the water weight by 3.535, assuming the specific gravity of hide substance to be 1.425. From the weight of hide substance the pelt can then be calculated, on the basis of a normal content of 80% of water, to the pelt weight. The weight of water free raw hide shows that the specific gravity of greenhide with hair is 1.45. Therefore the original "coming in" weight is obtained by multiplying the water weight of the hide by 3.216 and adding the weight of hair, flesh and water content. It was ascertained later by the author that the water weight had been determined long ago by H. R. Procter.

Vegetable Tanning Materials.

W. Möller[13] conducted an investigation on the tanning value of the black locust (*Robinia pseudoacacia*).

R. Lauffmann[14] compiled data on native and foreign tanning agents that formerly were principally used, also parts of a number of domestic plants containing tannin, that formerly were utilized but little if at all.

An anonymous author[15] in an article on the domestic sources of tannin, fat, oil and resin, gives the following data on tannin content of various materials: Oak bark, 6-17%; pine bark, 7-18; chestnut bark, 8-14; willow bark, 6-16; birch bark, 6-14; alder bark, 8-20; larch bark, 6-14; walnut bark, 3-12; acacia bark, 2.7; poplar bark, 5-11; aspen bark, 7; silver fir bark, 4-8; chestnut wood, 5-13; oakwood, 1-10; pine wood, 1-2; walnut wood, 1-10; acacia wood, 1-5; maple wood, 7; beech wood, 1; horse chestnut wood, 1; acorn cups, 6-13; oak galls, 7-9; oak twigs, 3-5; pine cones, 2-12; pine needles, 3-8; pine twigs, 4-7; alder fruit, 14; horse chestnut shells, brown interior, 6; walnut shells, exterior, dried, 9-22; heather, 3-14.

L. Pollak[16] gave data on the composition of the ash of a number of tanning materials and tanning extracts. Among others, the following average values were obtained on extracts (calculated on tannin)—Quebracho extract—0.15% chlorine, 0.25% magnesia; mangrove extract—2% chlorine, 0.70% magnesia; myrabolan extract—0.15% chlorine, 0.33 magnesia. Mangrove extract is distinguished by a higher content of chlorine and magnesia.

[12] *Leder-und Schuhmarkt*, 1918, No. 25. *Gerber*, 1918, 191 and 202.
[13] *Gerber*, 1918, 105. Abstr. this JOURNAL, **15**, — (1920).
[14] *Zeitsch. öffentl. Chemie*, 1918, 93.
[15] *Ledertechn. Ruud.*, 1918, 58.
[16] *Collegium*, 1918, 1.

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A process for obtaining tannin from pine bark, by L. Bruml and R. Silberberger (Ger. Pat. 306,529), is characterized by removing the resin with a solvent boiling at about 100° C. before leaching in the usual manner.

J. Herschfeldt[17] stated with reference to the bark peeling process of Gütschow wherein bark is peeled and dried simultaneously, that the process had the disadvantage of requiring coal and water in the forest and also that the quantity of bark peeled can not be dryed quickly enough. He suggests that this disadvantage would be removed, if the steaming, peeling and drying were carried out in the tanneries, providing these are near the source, or by cellulose manufacturers situated in the vicinity of tanneries.

Tannin Analysis. R. Lauffmann[18] has found that the vegetable tannins in the presence of hydrochloric acid yield condensation products with furfurol, that are either dark brown or black bodies; and that this reaction is useful in the same way as the formaldehyde reaction of Stiasny for the differentiation of the tannins, especially for the detection of pyrogallol tannin in the presence of protocatechol tannin. The former in case it is present can be detected in the filtrate after the addition of iron alum and sodium acetate by the appearance of a violet zone. By the determination of the quantity of the condensation product and calculating in the same manner as for the formaldehyde precipitation numbers, ascertained by the author (*Coll.* 161, 1917), it can be utilized for differentiation of tanning materials. The qualitative test for the tannins or the determination of the furfurol precipitation number is carried out in the following manner: 50 cc. of the clear tannin solution of analytical strength is mixed with 20 cc. each of a clear 70% furfurol solution and a 20% hydrochloric acid solution. The mixture is boiled one-half hour under a reflux condenser and filtered thru a weighed filter. The filtrate is tested by the addition of iron alum and sodium acetate for pyrogallol tannin. For the determination of the precipitation number, the precipitate is washed with hot water, the filter dried to constant weight and the weight of the precipitate calculated on 100 parts of soluble solids.

Lauffmann also discusses the detection and identification of vegetable tannins according to the earlier practical, useful methods;[19] the methods to be observed in sampling and testing of tanning materials and extracts, which can lead to faulty results;[20] and a further treatise[21] on the newer methods of tannin analysis and their practical value as compared with the hide powder method, in which he comes to the conclusion that all of these methods are really more bothersome and afflicted with more sources of error than the gravimetric hide powder method.

[17] *Lederindustrie,* 1918, No. 257.
[18] *Ledertechn. Ruud.,* 1918, 97. Abstr. this JOURNAL, 14, 470 (1919).
[19] *Zeitsch. öffentl. Chemie.,* 1918, 49.
[20] *Zeitsch. öffentl. Chemie.,* 1918, 135.
[21] *Ledertechn. Ruud.,* 1918, 33. Abst. this JOURNAL, 14, 81 (1919).

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W. Möller[22] describes an apparatus for extracting tanning materials which he thinks is an improvement over the apparatus of Teas, Grasser and all others.

VEGETABLE, MINERAL, CHAMOIS AND COMBINATION TANNAGES.

The manufacture of brown military leather is described anonymously.[23]

A tanning process by E. Kanet (Ger. Pat. 306,013) uses hydrolytically dissociated tanning solutions which separate on heating into basic salts, and alkali hydroxide, or oxide and is characterized by (1) tanning at lower temperatures with solutions made basic at the usual temperature or (2) letting a solution, which tans more or less completely or not at all, be absorbed by the hide at a relatively lower temperature and then raising the temperature. It is found that the stronger basic chromic oxide solutions and organic chrome compounds have the disadvantage of precipitating chromic hydroxide, especially when diluted, whereby the surface of the hide is quickly tanned and this tends to prevent penetration into the interior. If these solutions are cooled according to the proposed method they remain clear and are stable much longer. A solution cooled down in this manner tans thru uniformly and slower and offers the advantage that more basic solutions can be used, making the leather more plump and softer. With ferric salts, which at increased temperatures act on the hide, the process has the additional advantage that, by the use of lower temperatures, oxidation is hindered and injury to the hide is avoided. For iron tannage the process is carried out as follows: The pelts are brought into a solution of ferric acetate containing common salt or any electrolyte, as, sodium acetate for example. The most favorable concentration was found to be ½ to 2½% Fe_2O_3. After the hide has absorbed the liquor, it is taken out and thrown into a warm (45-60° C.) weak salt solution or hung up in a warm room, and after a short time the hides can be finished in the usual manner.

An anonymous treatise[24] describes the production of alum tanned Saddler's leather. The pickled pelts are treated with a solution of common salt and glaubers salt and then drummed with a basic solution of aluminum sulphate, oiled with a water soluble oil and finally supplied with a tawing paste as in producing glove kid leather. The leather is then set out on the grain side, brushed with a paste made of glycerin solution and talc, dried, dampened, staked again if necessary, powdered and rubbed off. Leather produced in this manner besides having a good appearance will possess a much greater resistance to water than ordinary tawed leather.

V. Mikuschka[25] describes the practical lines of procedure for the production of washable glove leather (white glove leather, Mocha and

[22] *Collegium*, 1918, 119. See also *Coll.* 1915, 195 and 292.
[23] *Gerber*, 1918, 149.
[24] *Gerber*, 1918, 75.
[25] *Gerber*, 1918, 45.

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Nappa leathers). The process consists of, first producing the usual glove kid and then making this washable by a subsequent treatment with formaldehyde, which must be preceded by a thorough washing. The capability of the leather to be washed increases with increasing concentration of the formaldehyde solution and with increasing temperature up to 75° C. In general a washable leather can be obtained at 80-85° C. without unfavorable influence on its properties. Oiling is carried out advantageously with prepared oils, "Elgon" is recommended by the author. The use of egg yolk is not to be recommended, since it produces light yellow flecks. Nappa leather, which supplied on a considerably higher requirement with reference to its ability to be washed, can be produced merely by chrome tanning but is much better when given an after treatment with formaldehyde. This is followed by retanning with vegetable tanning materials, mordenting and dyeing. Nappa leather produced in this manner possesses an unusually high resistance to washing and survives the temperature of boiling water. Similar processes are used for the production of Mocha and chair leathers. Here the leather is tanned as for glove kid, treated with formaldehyde, the egg yolk tannage is omitted, dressed in the usual manner and finally retanned with chrome.

According to German Patent 308,356 by O. Röhm, alum tannage is conducted with sulphonated oil together with flour. Three parts by weight of sulphonated oil, which is free from or poor in soap, is diluted with 30 parts by weight of water and 15 parts by weight of wheat flour is added while stirring. To this mixture is slowly added with constant stirring a solution of 6 parts alum, 2 parts salt and 30 parts water. The skins are drummed in this in the usual manner.

K. Schorlemmer (*Coll.* 1917, 345) has described the different methods for the determination of chromium in salt solutions and chrome residues and referred to the fact that the presence of iron exerts an influence on the determination. In a further work[26] Schorlemmer arrives at the following conclusions, on the basis of his researches. The presence of iron in a chrome salt solution, which will be oxidized with H_2O_2 in alkaline solution, has an influence on titration results by the thiosulphate and the spot method. It is possible to determine successfully the chromium quantitatively when in the presence of iron, if the oxidation is carried out by the addition of H_2O_2, then the precipitated ferric hydroxide filtered off; the precipitate dissolved in acid, this solution made alkaline and oxidized a second time with H_2O_2 and the iron filtered off. The combined filtrates contain all of the chrome as chromate. In the presence of very much iron, the iron precipitate is redissolved again and treated in the same manner. R. Lauffmann[27] has also investigated the influence of iron as well as organic matter on the chrome determination. In the iodometric determination with the use of Na_2O_2 as oxidizing agent, material amounts of ferric compounds give results that are too high. If large amounts of hydroxides precipitate in the oxidation which are filtered off

[26] *Collegium*, 1918, 145.

[27] *Ledertechn. Ruud.*, 1918, 37. Abst. this JOURNAL 14, 82 (1919).

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and washed, then the results obtained are too low, because this precipitate carries down and tenaciously retains chromate, so that it can not be washed out completely even by careful washing. If the solution for analysis contains large quantities of organic matter, then inexact results are obtained by the oxidation method with Na_2O_2, since this matter insofar as it is not oxidized, is detrimental to the liberation of iodine and also retards and makes the end point of the titration much more uncertain. If, besides chrome, material quantities of ferric compounds or organic matter are present, then the method with the oxidizing melt can be used; in the absence of organic matter, the method with ferrous ammonium sulphate. In the presence of organic matter one can undertake the oxidation of chrome and the destruction of organic matter with potassium permanganate and determine the chrome in the filtrate from the precipitated manganese hydroxide.

Other Tanning Materials and Methods.

W. Möller[28] replied to the objections raised against his peptisation theory of tanning by W. Fahrion (*Coll.* 1917, 320) and gives results of research which speak against the chemical theory of aldehyde tannage and serve as proof that the peptisation theory is also of importance in aldehyde tannage. Möller found that only the aliphatic aldehydes, which incline to polymerization and condensation, have a tanning effect, but not the aromatic aldehydes which do not show these properties. According to the chemical theory of tanning the aromatic aldehydes should tan as well, if not better (on account of their molecular weight) than the aliphatic aldehydes. According to Möller, the tanning process with aldehydes depends on the fact that the weak tanning property of the ordinary aldehyde solution is augmented by the addition of acids or alkalies when polymerization and condensation products are increased and accordingly a larger amount of peptised substance is produced.

W. Möller[29] explains the tannage with quinone by the aid of his peptisation theory. There occurs a partial conversion of quinones into colloidal humus matter, which is peptised by the unchanged quinone compounds, so that it is really a question of humus tanning.

Materials and Processes for Dressing and the After-Treatment of Leather.

Data is presented by an anonymous author[30] on domestic sources for fats, oils and resins. Niederstedt[31] also presents data on the oil content of kernels and seeds of domestic plants and furthermore describes the recovery of fat from sewage. There has been published the conclusion of a work by W. Fahrion on the "Tanner's Fatty Materials,"[32] which offers a compilation of the manifold usages of fats, their conversion products and fat-like substances in the production and preservation of leather.

[28] *Collegium,* 1918, 25.
[29] *Collegium,* 1918, 71.
[30] *Wellmarkt,* 1918, 128.
[31] *Ledertechn. Ruud.,* 1918, 58.
[32] *Gerber,* 1918, 13 and 30.

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J. Marcusson[33] obtained satisfactory results in the determination of the soap content of refined mineral oils, on which the usual titration method failed to work, by the following method: The solution is shaken out with 20 cc. 50% alcohol and the alcohol treatment repeated (about 7 times) until a test of the extract no longer shows a residue on evaporation. The united alcohol extracts are then shaken out with petroleum ether as by the method of Spitz and Hönig in order to remove occluded oil. The alcohol extract is then evaporated, the residue dried to constant weight, and the soap thus obtained is weighed.

F. Erban[34] found the usual method of fatty acid determination, in which the soap is decomposed in dilute aqueous solution and the fatty acids extracted with ether, to be difficult in the case of a heavily filled soap. An easier method is proposed where the soap is decomposed by acid in concentrated solution, sand is added if necessary and the whole evaporated to dryness on the water bath. The fatty constituents are then extracted from the filler and sand in a Soxhlet apparatus with ether. The use of nitrocellulose in the manufacture of leather is described anonymously.[35] F. Zimmer[36] reports on varnish and cellulose lacquers and their solvents and quotes a number of patented processes for their production.

According to a process by F. Natho (Ger. Pat. 302,158) an impregnating compound for leather is produced by mixing burgundy pitch, cumarone and similar resins, as well as animal fats, in different proportions according to the purpose for which it is intended. This mixture is then heated, vulcanized by the addition of sulphur, then cooled down to 30°-40° and diluted with volatile solvents, benzol or carbon tetrachloride.

According to German Pat. 300,908 a process for the production of japanned leather by the use of cellulose esters is described. Austrian pat. 73,689 by W. R. Schmith concerns a process and an appliance for the treatment by means of heat and light rays for drying or ripening japan coatings for leather and the like.

LEATHER.

W. Möller[37] found that the structure of hides or leather from seals, whales, reptiles and fishes differ materially from that of the animals, and a number of characteristics are described. The same author[38] traces the decomposition (brittle and cracky nature) of vegetable tanned leather on being stored mainly to the fact that the peptiser of the vegetable tanning material is changed by oxidizing agencies into colloidal humus matter (which also occurs when leather is allowed to heat). The solid solution of peptisers with hide substance is broken up and the fibrillar structure of the connective tissue fibers is changed in such a manner that the stability of the leather is injured. With iron leather, at least that produced by the older processes, the decrease in stability that occurs is

[33] *Chem. Umshau*, 1918, 2.

[34] *Mitteilungen des k. k. Techn. Versuchsamtes*, 1, 13 (1918).

[35] *Gerber*, 1918, 265.

[36] *Kunststoffe*, 1918, 92.

[37] *Gerber*, 1918, 1.

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usually traced back to the presence of free acid in the leather and decomposition of the iron compounds under the influence of oxidizing reactions, which occur easier in the acid than in the neutral or alkaline condition W. Röhm,[39] who, according to his communication has succeeded in producing a completely neutral iron leather, has determined directly the action of oxidizing agents on iron leather. He subjected neutral and acid iron leather to the action of hydrogen peroxide and compared their stability with one another. Röhm found that the neutral leather was much more resistant than the acid leather and that sulphuric and formic acid in like quantities are more injurious than hydrochloric.

M. Gonnerman,[40] in the investigation of vegetable tanned leathers among which were some samples of antique leather, always found a content of silica and alumina of from 20 to 41% of the total ash.

R. Lauffmann[41] gives a comprehensive description of the physical methods for testing leather, especially the determination of the wearing quality, the resistance to tear and tension and the resistance to water. F. Kopecky[42] in a treatise on war leather gives a critical description of conditions and directions for the mechanical testing of leather which served the military authorities as a basis for valuation.

C. Immerheiser[43] gives a method for the determination of free sulphuric acid in leather. J. Paessler[44] corroborates the method of Immerheiser, stating that he has obtained good results with it and describes the method of working. According to W. Möller[45] the method of Immerheiser contains a number of sources of error, which result in too low a content of free sulphuric acid, also of total sulphuric acid.

Artificial Leather and Leather Substitutes.

B. Köhnstein[46] reports in detail on the different leather substitutes during the war. R. Lauffmann[47] gives a short review of the recent patented processes and appliances concerning artificial soles and sole preservatives. Jaht likewise treats of the different substitute materials for soles especially the different forms of wooden soles,[48] and in another treatise[49] the use of leather waste for the production of cushion tires for bicycles in place of caoutchouc.

According to a process by O. Steiner (Ger. Pat. 304,497) for the production of leather substitute, spring netting for feather mattresses

[39] *Collegium*, 1918, 102.
[40] *Collegium*, 1918, 268.
[41] *Collegium*, 1918, 78.
[42] *Kunststoffe*, 1918, 85.
[43] *Gerber*, 1918, Nos. 1039, 1040 and 1046.
[44] *Ledertechn. Ruud.*, 1918, 81. Abst. this JOURNAL 14, 422 (1919).
[45] *Collegium*, 1918, 269.
[46] *Ledertechn. Ruud.*, 1918, 101.
[47] *Allgemeine Gerberzeitung*, 1918, Nos. 25 and 26.
[48] *Kunststoffe*, 1918, 25.
[49] *Kunststoffe*, 1918, 253.
[50] *Kunststoffe*, 1918, 157.

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are filled with cellulose, boiled in tar, dried and then coated with a mixture of wood and cellulose and dried under pressure. According to Ger. Pat. 307,582 by E. Wagner, leather substitute is produced from protein, protein like bodies, as bacteria, yeast, albumen and mixtures of these. According to a process by T. Schmid and J. Foltzer (Ger. Pat. 308,089) for the production of artificial leather and similar formed surfaces, a carded felt, fibrous mat is conducted thru a finishing machine, which rolls a cellulose solution into it under pressure and afterwards leads it thru a cellulose hardening fluid. Ger. Pat. 306,834 by H. Rhinow concerns a process for the production of leather like reliefs, whereby animal entrail skins are colored and then drawn while damp over a suitable base.

Waste and Sewage.

For the preparation of fleshings for glue making according to Ger. Pat. 303,184 by O. Röhm, they are first treated with protein splitting enzymes, if necessary with the addition of ammonium salts or other material which will neutralize lime or alkali. The fleshings, that are only attacked slowly by the enzymes, is swollen with a .5% caustic soda solution before treatment.

E. Guisiana[50] and an anonymous author[51] treat of the working up of residues of chrome tanning for the recovery of chrome for tanning and other purposes. Ger. Pat. 297,197 concerns the production of insulating material from leather waste for floor coverings.

F. Kopecky[52] in a treatise on tannnery sewage, describes the different kinds of sewage from the tannery, their handling and purification and recommends as a purification process the Kremer sedementation process.

Miscellaneous.

R. Kobert[53] reports on an ancient illustration of leather making from the year 1475 B. C. and draws from it that the history of cobblers knives, having the shape of a half moon, reaches back to the old Egyptian period. A. Gansser[54] gives further illucidating explanations of this illustration.

P. Martell[55] treats of the genealogy of domestic cattle and concludes that they descend from aurocks (*Bos primigenius*) according to the predominating conception of science.

Rubber gloves, which are much used in the tannery, according to an anonymous writer,[56] can be substituted by gloves that are treated with a mixture of 80 parts of casein glue solution and 9 parts of borax-shellac solution with addition of some castor oil. Then dip for a short time in formaldehyde and cover immediately with a mixture of glycerine and castor oil.

G. W. S.

[50] *Gerber*, 1918, 48. *Le Cuir* 5, 799.
[51] *Lederzeitung*, 1918, 586.
[52] *Gerber*, 1918, 133.
[53] *Collegium*, 1918, 117.
[54] *Collegium*, 1918, 198.
[55] *Collegium*, 1918, 10.
[56] *Collegium*, 1918, 282.

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THE

JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

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CONTENTS

Elections - - - - - - - - 267
Seventeenth Annual Meeting - - - - - - 268
Program - - - - - - - - 268
Complete Analysis of Chrome Leather—1920 Committee Report. By Louis E. Levi, Chairman - - - - - - 269
Total, Soluble and Insoluble Ash in Leather—1920 Committee Report. By J. M. Seltzer, Chairman - - - - - 270
The Retardation of Chrome Tanning by Neutral Salts. By John Arthur Wilson and Edwin A. Gallun - - - - - 273
The Analysis of Sulphonated Oils—1920 Committee Report. By G. W. Schultz, Chairman - - - - - - 283
The True Tanning Value of Vegetable Tanning Materials. By John Arthur Wilson and Erwin J. Kern - - - - - - 295
Committee on Limeyard Control. I. The Analysis of Lime Liquors. By Donald Burton - - - - - - - 308
Hydration as an Explanation of the Neutral Salts Effect. By John Arthur Wilson - - - - - - - - 323
Abstracts - - - - - - - - 330
Patents - - - - - - - - 336

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G. W. SCHULTZ . . . . . Associate Editor

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ELECTIONS.

ACTIVE.

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J. Alexander, % The J. S. Young Co., 2701 Boston St., Baltimore, Md.

ASSOCIATE.

E. R. McKee, % International Products Co., Casillo Correo 152, Asuncion, Paraguay.

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SEVENTEENTH ANNUAL MEETING.

The seventeenth annual meeting of the A. L. C. A. will be held at the Marlborough Blenheim, Atlantic City, N. J., on May 27, 28 and 29th.

Owing to the unusally crowded conditions at Atlantic City it is suggested that each member communicate direct with the management of the Marlborough Blenheim, as early as possible.

The schedule of rates is as follows:

	American plan per day	European plan per day
Single rooms without bath (one person)....	$8	$5
Single rooms with bath (one person).....	$10, $11, $12	$7, $8, $9
Double rooms without bath (two persons)...	$14	$7
Double rooms with bath (two persons).....	$16, $18, $21 to $25	$9, $11, $14 to $18

PROGRAM.

The program of the annual meeting is still in the course of construction and up to the time this issue went to press the subjects to be presented were as follows:

President's Address.....Robert W. Griffith

Committee Reports.

The True Tanning Value of Vegetable Tanning Materials
John Arthur Wilson and Erwin J. Kern

The Direct Measurement of the Plumping Powers of Tan Liquors
Alan A. Claflin

A New Method for the Determination of Sulphuric Acid in Leather
Dr. Arthur W. Thomas

Hide Substance.....G. L. Terrasse

The Retardation of Chrome Tanning by Neutral Salts
John Arthur Wilson and Edwin A. Gallun

Time Factor in the Adsorption of the Constituents of Chromic Sulphate Solutions by Hide Powder
Dr. A. W. Thomas and Margaret W. Kelly

The Effect of Humidity on the Strength and Stretch of Leather
F. P. Veitch and M. G. Hunt

Unhairing of Hides and Skins by Enzyme Action.....Dr. C. S. Hollander

The Titration of Chrome Liquors by the Conductance Method
Dr. A. W. Thomas and Stuart B. Foster

The Commercial Application of the Work of the Forest Products Laboratory .....Forest Products Laboratory

Some New Development in the Production of Tanning Extracts from Waste Sulphite Liquor.....Walter H. Dickerson

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COMPLETE ANALYSIS OF CHROME LEATHER— 1920 COMMITTEE REPORT.

By Louis E. Levi, Chairman.

The Committee consisted of the following: Louis E. Levi, Chairman; T. P. Hou, A. C. Orthmann, H. L. Pierson, P. T. Tarouski, J. R. Lorenz, Thos. Harrington, F. P. Veitch.

Messrs. Levi, Hou, Orthmann, Tarouski, Lorenz and Harrington making a full report on the work outlined, recommend that the following methods be adopted by the American Leather Chemists Association.

Messrs. Veitch and Pierson, not reporting.

Moisture:—Same as American Leather Chemists Association's Method for Vegetable analysis, 1919.

Fat:—Extract 10 grams of the air dried leather in a Soxhlet apparatus for a period of 8 hours with petroleum ether having a boiling point of no more than 80° C. Evaporate off solvent and dry for ½ hour at 105° C.

Ash:—Ignite 3 grams of the leather in a tared, silica, porcelain or platinum crucible over a low flame until all organic matter is destroyed, then continue ignition over high flame until thoroughly ashed. Cool in dessicator and weigh.

Iron, Aluminum, Chromium:—"A"—Remove the ash to a platinum crucible and mix intimately with 4 grams of fusion mixture made of equal parts of Potassium Carbonate, Sodium Carbonate and Borax glass (all must be free from Fe & Al) and fuse for a period of 30 minutes over a strong Bunsen flame. After fusing place crucible and contents in a 150 cc. beaker, dissolve in hot water and add HCl, in excess. If any undissolved residue remains, filter, wash, ignite filter and fuse residue a second time, as above. Combine both fusion solutions, then add slight excess of NH_4OH, bring to a boil, filter, wash well, dry and ignite, as $3Fe_2O_3 + Al_2O_3$. The filtrate is cooled and diluted to 500 cc. 100 cc. of this dilution is placed into an Erlenmeyer flask, enough conc. HCl to neutralize and leave 5 cc. in excess is added, then 15 cc. of 10% KI is added, allowed to stand about one minute and titrated with N/10 Sodium Hyposulfite, using starch as indicator.

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"B"—If it is not desired to determine Fe or Al, the ash of 3 grams of leather may be transferred to an iron crucible, mixed with 5 grams of sodium peroxide and fused 10 minutes. Place cooled crucible in 300 cc. water in a casserole and boil 20 minutes. Wash into a 500 cc. flask, cool and make up to the mark. Filter through a dry filter. Place 100 cc. of filtrate in Erlenmeyer flask, neutralize with HCl, add 5 cc. excess and proceed as in "A."

Lime:—Take 200 cc. of the dilution from "A", heat to boiling, add 10 cc. of hot 10% Ammonium Oxalate solution, allow to stand 4 hours, filter and wash well with hot water, dry, ignite and weigh as CaO.

Nitrogen:—Same as American Leather Chemists Association's Method for Vegetable Leather analysis, 1919.

Total Sulfate:—The reagent: Take 50 grams of C. P. Potassium Bichromate and dissolve in 150 cc. of water. When dissolved add 50 cc. of C. P. conc. HCl. Weigh out 1 gram of fat free leather into a 250 cc. beaker and add 20 cc. of the reagent and bring to a gentle boil. Then add 8 to 10 cc. of HCl, let digest over burner until all organic matter is destroyed. Boil vigorously for 2 or 3 minutes after which add about 50 cc. water and about 5 cc. of alcohol. Boil until all chrome is reduced and alcohol and aldehyde is driven off. Add 50 cc. more water, bring to a boil and add barium chloride solution, let stand 2 or 3 hours. Filter and wash precipitate, burn in tared crucible, cool and weigh.

Calculate weight of $BaSO_4$ to SO_3.

TOTAL, SOLUBLE AND INSOLUBLE ASH IN LEATHER—1920 COMMITTEE REPORT.

By J. M. Seltzer, Chairman.

It was decided that no analytical work would be done this year but comments should be made by the collaborators of the 1919 Committee based on the results of their investigation made at that time.

The following letter was sent out by the Chairman.

The committee on "Total, Soluble and Insoluble Ash in Leather" has been asked to comment on the following method of reporting the ash percentage in leather.

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(1) Determine ash in leather after the extraction of the water soluble. Call this ash, insoluble ash.

(2) Burn aliquot portion of water soluble and determine the ash. Call this, soluble ash.

Sum of one and two equal total ash.

One is the figure that should be used in items summing up to 100%, the total ash and two not included in the 100%.

No samples will be sent out for analysis, but the chairman would suggest that the following articles be read and your comments based on these former committee reports in addition to any other information which you may have at hand.

J. A. L. C. A. Vol. 14, pages 243-255, 443-450, and Vol. 15, pages 130-133.

The following replies were received from the collaborators.

W. K. ALSOP: I think the determination of the ash, as in (1), advisable especially if it is intended to attempt to calculate the combined tannin from the analysis of the leather. I do not think it is very material whether the total ash is made by burning an aliquot portion of the water soluble, adding this to the result obtained by (1) or whether the leather is ashed directly. Neither one gives the actual amount of the mineral salts as they are in the leather, and it seems to me that it would be simpler to ash the leather direct than to make the other determination.

E. J. KERN: Nothing further to report.

V. MLEJNEK: As most of the collaborators of the last year agreed, the sum of the ash from the water extractive and the ash from the extracted leather represents a much truer total ash figure than that obtained by direct ashing of the original leather. This is due apparently to the relatively small amount of organic matter present in the extractive to cause a reduction of mineral matter from salt to base during the process of ashing.

The ash obtained from the extracted leather is relatively small in a vegetable tanned leather so that any amount of reduction could in no event seriously alter that result.

We believe that in an analysis of leather one (1) should be included in the total when summing up to 100%, and that two (2) should not be included therein. However, it is our opinion that in reporting a leather analysis mention should be made of the

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extractive ash in order to give some measure of the water soluble mineral matter.

F. F. MARSHALL AND T. LOWRY: We believe that the method as outlined by the Chairman *i. e.*

(1) Determine ash in leather after the extraction of the water soluble. Call this ash, insoluble ash.

(2) Burn aliquot portion of water soluble and determine ash. Call this ash, soluble ash.

Sum of one and two equals total ash.

To be the correct method of determining the total, soluble and insoluble ash in leather.

J. S. ROGERS: The results for insoluble ash obtained by ashing the leather residue left after the water extraction were in reasonably good agreement, and I believe that this method for determination of insoluble ash is satisfactory.

The results for soluble ash obtained by ashing a portion of the evaporated water soluble material were not concordant. There is indication that in this procedure there is some reduction of sulphates, although this is not as great as that which occurs in ashing the original leather. This lack of concordance is probably due to the variation in the amount of reduction as obtained by somewhat different conditions of ashing. These results are not as concordant as those obtained by ashing the original leather. I believe therefore, that unless a procedure for determining insoluble ash can be developed which will eliminate reduction, that more concordant and just as valuable results for total ash can be obtained by ashing the original sample. If a procedure can be developed which will prevent reduction in determining insoluble ash, I believe that the total ash value obtained from the sum of the insoluble ash, and the soluble ash (determined without reduction) would be the preferable method for reporting.

G. L. TERRASSE: The error involved in first subtracting from one hundred the soluble parts of the ash obtained in burning the original leather and again by subtracting the soluble ash obtained as solids from the original leather in the aqueous extractive, was apparently first noted by Proctor himself. The error appears to have inadvertently crept in, in originally suggesting the approximate correct method of determining the degree of tannage by Von Schroeder. A discussion of this phase of the question

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is admirably handled in an article by Parker and Paul reprinted in 1910 in this JOURNAL, volume 5, page 305.

It is obvious that if the ash in leather is determined after the extraction of water soluble, a figure is obtained which can be considered insoluble ash. If an aliquot part of the water soluble of the same leather be evaporated and burned this may rationally be called soluble ash. Again it is apparent that the sum of these two determinations may be considered the total ash. The first result obtained should plainly be used in summing up to one hundred per cent. and equally plainly the second should not be included for it has already been counted once in the total water soluble.

This leaves, entirely open for your committee's judgment, the questions as to the proper methods of procedure to secure these figures the answer merely considering the question of the proper method of calculation.

Chairman: All of the collaborators have agreed that Method (1) is satisfactory for determination of "Insoluble Ash" and the greater number that Method (2) is satisfactory for determination of "Soluble Ash", but believe that ignition for Soluble Ash should be made at the lowest possible temperature to eliminate the reduction of magnesium sulphate to the lowest degree, and that "Total Ash" should be the sum of (1) and (2).

THE RETARDATION OF CHROME TANNING BY NEUTRAL SALTS.

By John Arthur Wilson and Edwin A. Gallun.

Received April 5, 1920.

That the properties of a chrome liquor are markedly changed in many respects by the addition of neutral salts has been clearly demonstrated in the literature[1] of the past three years. It has also been shown[2] that, if common salt be added to a chrome liquor, the rate of tanning is reduced and the addition of a greater amount of alkali is required to produce complete tannage. The object of the present work was to investigate further this influence of neutral salts upon chrome tanning, and for this pur-

[1] Wilson and Kern, This JOURNAL 12, 445 (1917); Procter and Griffith, *Ibid.* 12, 612 (1917); Thomas and Baldwin, *Ibid.* 13, 248 (1918); Baldwin, *Ibid.* 14, 10 (1919); Thomas and Baldwin, *J. A. C. S.* 41, 1981 (1919).

[2] Wilson, *J. A. C. S.*, 42, 715 (1920.)

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pose sodium sulfate and the chlorides of ammonium, sodium, lithium, and magnesium were selected because they represent salts covering a wide range in degrees of hydration in aqueous solution.

The chromium compound used was a standard commercial product of the following composition:

Chromium salts (as Cr_2O_3)	24.2%
Aluminum salts (as Al_2O_3)	2.7%
Iron salts (as Fe_2O_3)	0.6%
Hydrolyzable sulfate (as SO_3)	21.0%
Sodium sulfate (as Na_2SO_4)	32.8%
Sodium chloride	0.6%

In the first series of experiments, solutions of this material were mixed with prepared salt solutions to give liquors containing in each case exactly 10 grams of chromic oxide per liter and salt as noted in Table I. A portion of pickled calfskin was cut into pieces, each 16 square inches in area, and one piece was put into each of 16 wide-mouth bottles along with 200 cc. of the chrome liquor to be studied. The bottles were then shaken in rotating boxes at intervals during 3 days. The pieces were then washed by shaking with successive changes of water until the wash water gave no appreciable tests for chlorides or sulfates in the cold. Strips of equal area were cut from each piece and immersed in boiling water for 5 minutes in order to determine the nearness to complete tannage. The remaining portions were cut into small pieces, dried, and analyzed for chromic oxide and hide substance. The chromic oxide was determined by ashing, fusing the ash with sodium carbonate and magnesium oxide, dissolving in dilute acid, and titrating with standard thiosulfate as usual. The per cent. of hide substance was taken as 5.62 times the per cent. of nitrogen as found by the Kjeldahl method. The results, in terms of the number of grams of chromic oxide combined with 100 grams of hide substance, are given in Table I and shown graphically in Figure I. The only piece which was fully tanned, as indicated by the boiling test, was the one from the liquor containing no added salt. In general, the appearance of the pieces after boiling followed the order of the analyses, those containing more chromic oxide standing the test better than those with less; the piece from the 3-M ammonium chloride liquor was badly shriveled and very dark in color.

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FIGURE I.

SHOWING HOW NEUTRAL SALTS RETARD THE CHROME TANNING OF PICKLED CALFSKIN IN A LIQUOR CONTAINING 10 GRAMS OF CHROMIC OXIDE PER LITER.

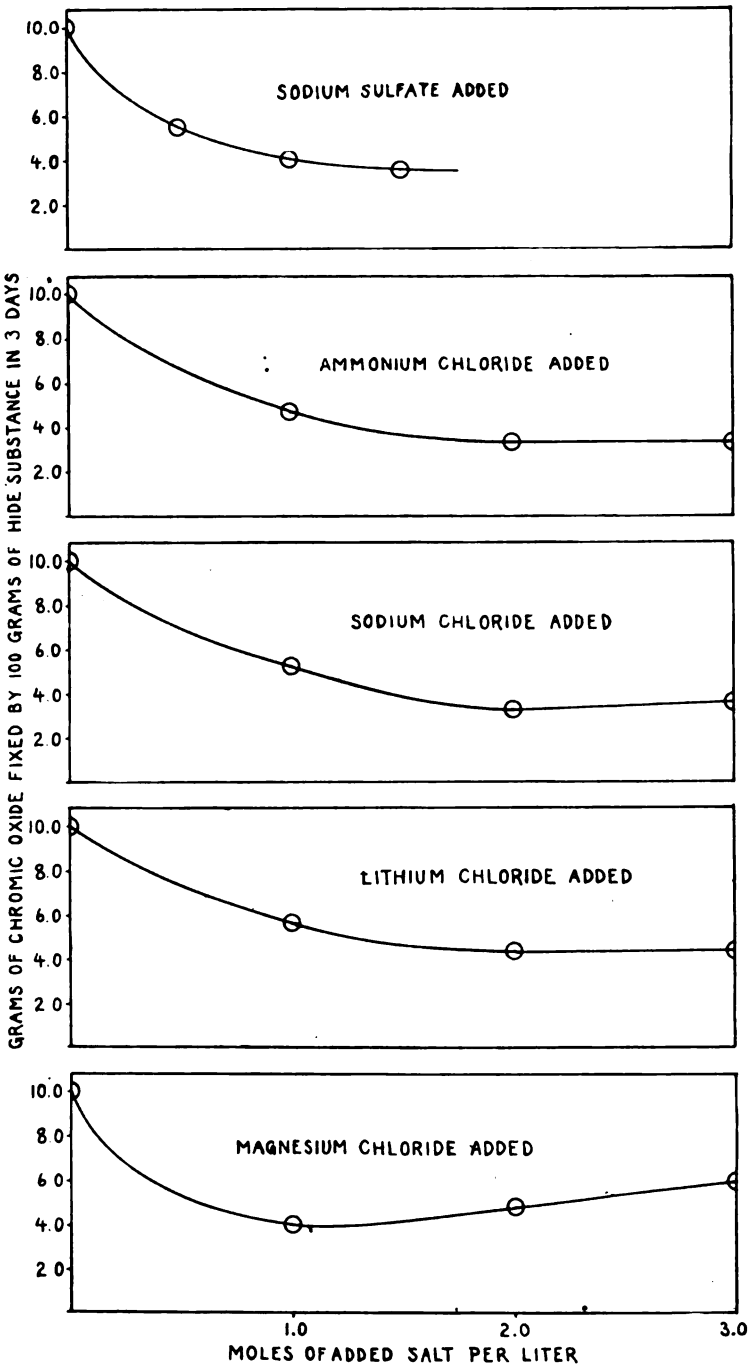

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FIGURE II.

SHOWING HOW NEUTRAL SALTS RETARD THE CHROME TANNING OF PICKLED CALFSKIN IN A LIQUOR CONTAINING 17 GRAMS OF CHROMIC OXIDE PER LITER.

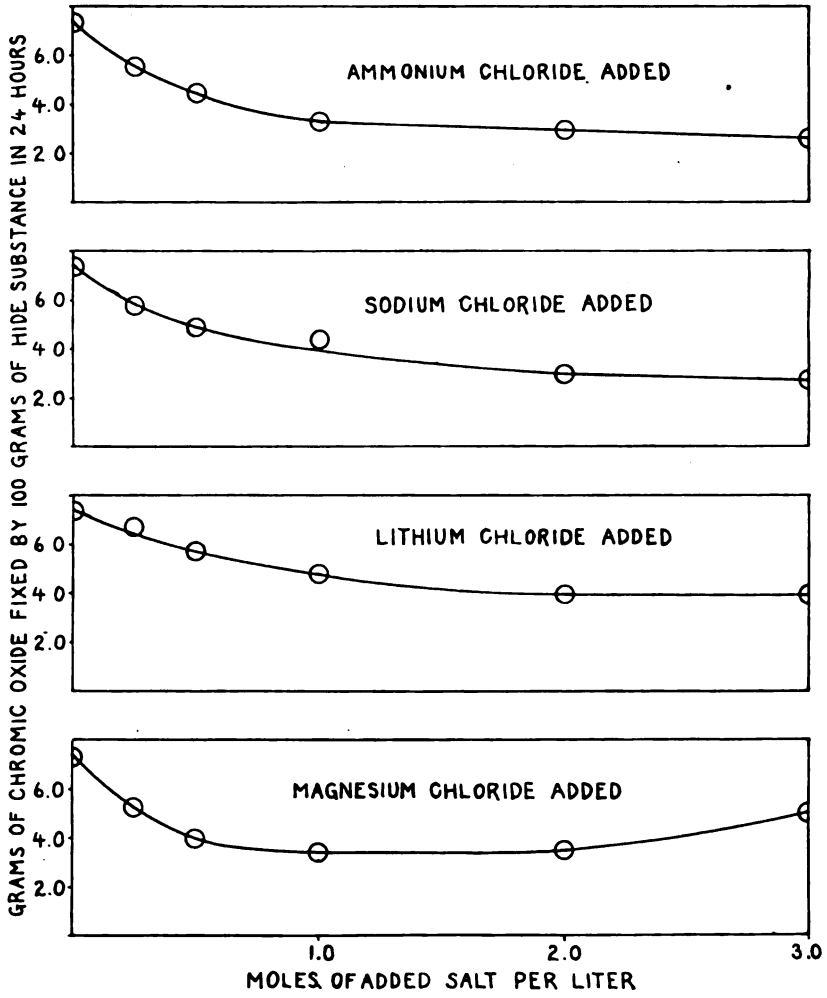

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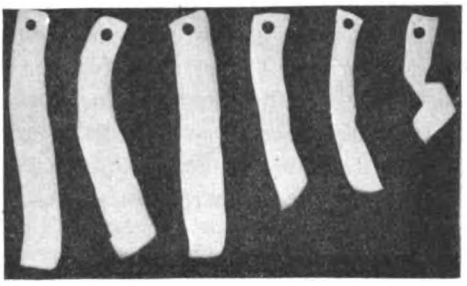
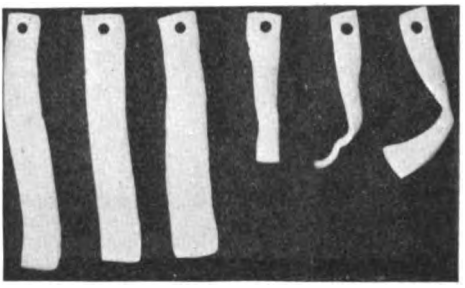
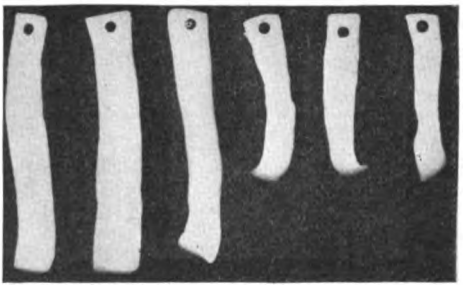
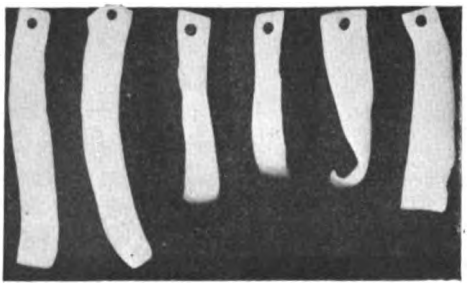
FIGURE III

SHOWING STRIPS OF THE LEATHER NOTED IN TABLE II, ALL ORIGINALLY OF EQUAL AREA, TAKEN AFTER IMMERSION IN BOILING WATER FOR 5 MINUTES AND DRYING.

KIND OF SALT	MOLES OF ADDED SALT PER LITER					
	NONE	0.25	0 50	1 00	2 00	3 00
AMMONIUM CHLORIDE						
SODIUM CHLORIDE						
LITHIUM CHLORIDE						
MAGNESIUM CHLORIDE						

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In the second series, the concentration of chromic oxide was raised to 17 grams per liter and the pieces of calfskin were allowed to remain in the liquors only 24 hours, this being sufficient for complete tannage of the piece in the liquor containing no added salt. The general procedure followed was the same as in the first series. The results of analysis are shown in Table II and Figure II. In Figure III are shown pictures of the strips, all originally of equal area and shape, taken after immersion in boiling water for 5 minutes and drying.

TABLE I.—SHOWING THE NUMBER OF GRAMS OF CHROMIC OXIDE FIXED BY 100 GRAMS OF HIDE SUBSTANCE IN 3 DAYS FROM A CHROME LIQUOR CONTAINING 10 GRAMS OF CHROMIC OXIDE PER LITER AND SALT AS NOTED IN THE TABLE.

moles of added salt per liter	sodium sulfate	ammonium chloride	sodium chloride	lithium chloride	magnesium chloride
none	10.09	10.09	10.09	10.09	10.09
0.50	5.50	—	—	—	—
1.00	4.07	4.68	5.19	5.62	4.03
1.50	3.57*	—	—	—	—
2.00	—	3.28	3.22	4.32	4.82
3.00	—	3.27	3.60	4.34	5.91

* Sodium sulfate had begun to crystallize out from the liquor.

TABLE II.—SHOWING THE NUMBER OF GRAMS OF CHROMIC OXIDE FIXED BY 100 GRAMS OF HIDE SUBSTANCE IN 24 HOURS FROM A CHROME LIQUOR CONTAINING 17 GRAMS OF CHROMIC OXIDE PER LITER AND SALT AS NOTED IN THE TABLE.

moles of added salt per liter	ammonium chloride	sodium chloride	lithium chloride	magnesium chloride
none	7 35	7.35	7.35	7.35
0.25	5.53	5.70	6.78	5.22
0.50	4.42	4.90	5.72	3.96
1.00	3.25	4.45	4.80	3.41
2.00	2.95	2.97	3.91	3.54
3.00	2.57	2.73	3.98	4.96

THEORETICAL DISCUSSION

Neutral salts play an extremely complicated role in chrome tanning and certain investigations are being conducted in the hope that a thorough understanding of their actions will bring about their much more efficient use. Although substantial progress has recently been made, particularly through the researches of Thomas and Baldwin, several points still remain obscure. However, the success which has already attended the method of research employed in this work gives promise of early and complete solution of this problem, at least from a practical standpoint.

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While this method is so commonly employed in research as hardly to require description, nevertheless it is so important as to warrant a detailed review of its application to the present problem.

The first step is to collect whatever data is available and form from these possibly several hypotheses, each of which is then subjected to the rigid test of experiment. Certain ideas are disproved and at once eliminated, while others are confirmed and furnish a basis for creating new and sounder hypotheses. A continuation of this process finally results in a good theory.

The present series of investigations began with the work of Wilson and Kern, who showed that the amount of alkali required to start precipitation in a given chrome liquor is increased by the addition of neutral salts and that the order of effectiveness in preventing precipitation, for the different salts when added in the proportion of 2 moles of salt to one liter of chrome liquor, is as follows:

$$KCl < NH_4Cl < NaCl < MgCl_2 < MgSO_4 < Na_2SO_4 < (NH_4)_2SO_4.$$

Only 4.0 cc. of N/10 NaOH was required to start precipitation of the chrome in 10 cc. of the liquor containing potassium chloride against 11.6 cc. for the one containing ammonium sulfate.

Because the order of these salts is practically the same as that for increasing degree of hydration in aqueous solution, Wilson and Kern put forth the hypothesis that the results obtained with chrome liquors were due chiefly to the hydration of the added salt. This view appeared reasonable, since any water which entered into combination with the salt would no longer be available as solvent, and thus the ratio of moles of free acid to moles of solvent would be increased, the more so the greater the degree of hydration of the added salt, and consequently more alkali would be required to start precipitation.

In a series of experiments with the hydrogen electrode, Thomas and Baldwin confirmed this hypothesis for chlorides, but showed it to be quite untenable for sulfates, which actually *lower* the hydrogen-ion concentration of chrome liquors. The very different behavior of chlorides and sulfates made it advisable to treat them separately in further reasoning.

The next step in testing the hydration hypothesis for chlorides was to examine the effect of neutral chlorides upon pure acid

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solutions. If the action of these salts upon chrome liquors is due to hydration, they should not only increase the hydrogen-ion concentration of acid solutions in accordance with their degrees of hydration, but they should increase it to a greater extent than in the case of chrome liquors, where some of the increase in hydrogen-ion concentration would be offset by repression of the hydrolysis of the chrome. The experimental results obtained by Thomas and Baldwin again fully confirmed the hypothesis.

But the reduction of the problem simply to that of determining the action of the salts upon pure acid solutions made possible a critical test of the hypothesis, since it should be possible, by noting the rise in concentration of hydrogen ion upon the addition of different amounts of salt to suitable acid solutions, to calculate the degree of hydration of the salt at any concentration. These calculations, which were recently made by one of us[3], in terms of moles of water combined with one mole of salt at infinite dilution, are in excellent agreement with similar calculations made by Smith[4], from data of a very different type. It therefore seems reasonable to conclude that the peculiar action of neutral chlorides upon chrome liquors, which we have noted, is due chiefly to the hydration of the added salt.

The action of sulfates upon chrome liquors is evidently more complicated. They lower the hydrogen-ion concentration of pure acid solutions, as well as of chrome liquors, which may be attributed to two different causes, one the repression of ionization of the acid and the other the formation of addition compounds between the salt and acid, but of these two possibilities, the latter appears much the more likely. Their action upon chrome liquors seems to be due to the formation of addition compounds between chromium salt and the sulfate as well as between the acid and added sulfate. It also appears probable that hydration of the added sulfate plays a part, since the hydrogen-ion concentration of the chrome liquor falls to a minimum and then rises with further increase in concentration of the salt.

At the time of starting the present investigation, we outlined, first of all, the results which we expected to get by adding the several chloride salts to the chrome liquor. No attempt was

[3] Wilson, *loc. cit.*

[4] *J. A. C. S.* 37, 722 (1915).

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made to predict results for the sulfate. A glance at Miss Baldwin's results[5] for the effect of concentration of a chrome liquor upon the amount of chromic oxide fixed per unit of hide substance shows that the maximum amount of chrome is fixed at a concentration of about 15 grams of chromic oxide per liter. The drop in amount of chrome fixed for the stronger solutions was attributed to the increasing concentration of hydrogen ion. Since the hydration of the added salts causes a concentrating effect upon all of the constituents of the chrome liquor, we expected each salt to retard the tanning to a greater extent with increasing concentration of salt, but that the order of effectiveness of the different salts, in retarding tanning, at the same concentration would be

$$NH_4Cl < NaCl < LiCl < MgCl_2.$$

Reasoning from the hydration values of these salts, we expected the differences due to concentration of the salt to be comparatively very great and the differences between the chlorides of ammonium, sodium, and lithium at the same concentration to be small, but unmistakably in the order noted.

The results given in Tables I and II show that the large retarding effect due to concentration is as we expected, but the smaller differences in effect between the different salts at the same concentration are not at all in the expected order, although the differences in the results for NH_4Cl, NaCl, and LiCl at equal concentrations are not great. The peculiar minimum for magnesium chloride shown in Figures I and II and beautifully illustrated in Figure III was quite unexpected.

The differences in action of the different salts is admittedly puzzling, but if we take the results for the molar concentrations in Table I, we find the following order for effectiveness in preventing tanning

$$MgCl_2 > NH_4Cl > NaCl > LiCl.$$

Professor Thomas points out that this is exactly the same order that Pauli found[6] for the effectiveness of salts in coagulating electropositive albumin. Since our chrome liquor was decidedly acid in reaction, our collagen would be electropositive. Whether the similarity of these two actions indicates a definite relation or

[5] This JOURNAL, 14, 439, (1919).

[6] cf. Robertson's *Physical Chemistry of the Proteins*, p. 120.

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is merely a coincidence remains for future experiment to decide.

A possible explanation of the minimum in the magnesium chloride curve lies in the extremely high degree of hydration of this salt. Miss Baldwin's work, just referred to, was carried out only up to a concentration of 66.4 grams of chromic oxide per liter, although at this point the amount of chrome fixed was still falling with increasing concentration. From hydration values now at hand, it appears unlikely that the addition of three moles per liter of NH_4Cl, NaCl, or LiCl would increase the concentration of even our stronger chrome liquor much above that of the strongest liquor used by Miss Baldwin. But, in the case of three-molar, and even two-molar, magnesium chloride, the concentrating effect due to hydration must be enormous. Although the increasing concentration of hydrogen ion may oppose the tanning action, it is probable that the increasing concentration of chrome favors it. Furthermore, with increasing concentration, the hydrolysis of the chrome by which the free acid is formed would be repressed. It is therefore quite possible that, had Miss Baldwin's experiments been carried further, say to 120 grams of chromic oxide per liter, a point of minimum would have been found beyond which increasing concentration would have caused greater fixation of chrome. Should this prove true, a good explanation of the magnesium chloride curve will have been found, and the prediction might then be made that all chlorides would show similar points of minimum if their concentrations in the chrome liquor were, or could be, made sufficiently great. This hypothesis will be tested as soon as the opportunity affords.

Practical Summary

The above results show that sodium sulfate, ammonium chloride, sodium chloride, lithium chloride, and magnesium chloride all retard chrome tanning to an extent depending upon their concentration in the chrome liquor, at least up to three-molar. With magnesium chloride, the greatest retarding influence is found at about molar concentration. The fact that the action of the added salt was similar in both series, the one in which a weak liquor was run for three days and the other in which a stronger liquor was run for only one day, suggests that

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the same behavior may be expected with any general type of chrome liquor.

It is very important to note that in any one series the concentration of chromic oxide and so-called basicity are the same for all liquors, but the rates of tanning are vastly different; in the first series the addition of one pound of common salt per gallon of chrome liquor reduced the number of grams of chromic oxide fixed by 100 grams of hide substance in three days from 10.09 to 3.22. This shows quite clearly that control of the neutral salt content of a chrome liquor ranks in importance with the proper control of basicity and that difficulties may easily arise from judging a liquor solely by its chromium content and basicity and ignoring its content of neutral salts.

Acknowledgement is made of the assistance of Messrs. Rudolph Olson and Roderick Bott.

Milwaukee, Wis.

THE ANALYSIS OF SULPHONATED OILS— 1920 COMMITTEE REPORT.

By G. W. Schultz, Chairman.

The work of the committee for this year was along the same lines as that of last year, with the exception that work was confined entirely to the determinations of combined SO_3, total fatty matter and neutral fat.

For the work on combined SO_3, three samples of sulphonated oil were prepared and supplied to the members of the committee with the following instructions:—

INSTRUCTIONS FOR SAMPLES NO. 1, 2, & 3.

METHOD A.

Each determination is to be run in duplicate.

Total Alkali:—Weigh 10 grams into a 250 cc. Erlenmeyer, dissolve in 150 cc. water (warm if necessary to effect solution). Titrate with N/2 H_2SO_4 using 5 cc. of methyl orange as indicator.

Calculated to milligrams KOH per gram = A

Combined SO_3:—Weigh 8 grams into a 300 cc. Erlenmeyer and boil for 1 hour with 25 cc. of N/2 H_2SO_4 under a reflux

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(use glass beads to prevent bumping, and shake frequently). Wash condenser into flask. To the cooled mixture add about 20 cc. of ether, 100 cc. distilled water, 25 cc. concentrated salt solution and 5 cc. methyl orange. Titrate with N/2 NaOH (stopper flask and shake well frequently).

cc. N/2 NaOH — 25 cc. N/2 H_2SO_4 = cc. N/2 H_2SO_4 liberated —this calculated to milligrams KOH per gram = F

$$\text{Then combined } SO_3 = \frac{(F + A)\,8}{56.1}.$$

METHOD B.

Each determination to be run in duplicate.

Total SO_3—Weigh 4 grams into an Erlenmeyer and boil for 40 minutes with 30 cc. HCl (1:15) under a reflux. Shake frequently. Cool, transfer to a separatory funnel and shake out with ethyl ether, draw off aqueous layer and wash ethereal layer three times with 25 cc. of water (using dilute HCl if necessary to break emulsions). Combine aqueous extracts, boil, filter and determine sulphuric acid as barium sulphate. Calculate to % SO_3 = (a).

SO_3 as Salts:—Dissolve 8 grams in about 100 cc. ether, wash, first with 75 cc. conc. salt solution free from sulphates, then twice with 25 cc. of salt solution. (Allow all washings to stand until the aqueous layer is clear). Combine washings, acidify with HCl and boil, filter and determine sulphuric acid as barium sulphate. Calculate to % SO_3 = (b).

Per cent. combined SO_3 = (a) — (b).

The determinations outlined under method A are those proposed by Hart; those under method B are the present provisional methods of the Association. The average of the results returned according to these instructions are given in Table I. It will be noted that the agreement between the different members of the committee is, in general, very good for both methods. Table II gives a comparison of the average analyses of the three samples by both methods, with the calculated analyses of samples No. 2 & 3 computed from the average analysis of No. 1 and the known additions. The agreement between the average and calculated analyses is good in both cases but is best in method B. And it

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will be noted that the values for combined SO_3 by method A is about 0.12% lower in every case excepting the average analysis for sample No. 3 where it is 0.20% lower.

TABLE I.

METHOD A.

	Vaudreuil	Cuthbert	Pierson	Hart and Liberthson	Bumcke	Schultz	Average	Greatest difference
Sample No. 1.								
Total alkali	7.89	7.90	8.60	8.50	7.90	8.50	8.21	0.71
Combined SO_3 ...	3.12	3.23	3.39	3.23	3.33	3.31	3.27	0.27
Sample No. 2.								
Total alkali	7.91	7.51	7.90	8.20	7.38	8.20	7.85	0.69
Combined SO_3 ...	3.01	3.12	3.08	3.17	3.05	3.17	3.10	0.16
Sample No. 3.								
Total alkali	7.47	7.05	7.50	8.30	6.91	7.60	7.47	1.39
Combined SO_3 ...	2.83	2.93	2.97	3.00	2.98	3.03	2.94	0.20
METHOD B.								
Sample No. 1.								
Total SO_3	3.90	3.93	4.04	4.18	3.98	3.94	4.00	0.28
SO_3 as salts.....	0.47	0.61	0.64	0.76	0.63	0.56	0.61	0.29
Combined SO_3 ...	3.43	3.32	3.40	3.42	3.35	3.38	3.39	0.11
Sample No. 2.								
Total SO_3	3.93	3.96	4.08	4.02	4.04	3.94	4.00	0.15
SO_3 as salts.....	0.75	0.79	0.83	0.64	0.85	0.84	0.78	0.20
Combined SO_3 ...	3.18	3.17	3.25	3.38	3.19	3.10	3.22	0.28
Sample No. 3.								
Total SO_3	3.90	4.06	4.14	4.23	4.08	4.01	4.07	0.33
SO_3 as salts.....	0.91	0.98	0.77	0.89	0.98	1.05	0.93	0.28
Combined SO_3 ...	2.99	3.08	3.37	3.34	3.09	2.96	3.14	0.41

TABLE II.

METHOD A.

	Sample No. 1. Average analysis	Sample No. 2. Average analysis	Sample No. 2. Calculated from No. 1.	Sample No. 3	
				Average analysis	Calculated from No. 1.
Total alkali	8.21	7.85	7.91	7.47	7.65
Combined SO_3	3.27	3.10	3.15	2.94	3.04
METHOD B.					
Total SO_3	4.00	4.00	4.05	4.07	4.11
SO_3 as salts.....	0.61	0.78	0.80	0.93	0.95
Combined SO_3	3.39	3.22	3.25	3.14	3.16

Sample No. 1 was a sulphonated cod oil.

Sample No. 2 was made of No. 1 + 3.78% of an aqueous sodium sulphate solution containing 5.56% SO_3.

Sample No. 3 was made of No. 1 + 7.33% of the same sodium sulphate solution.

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In order to compare the results to be obtained for total fatty matter and neutral fat by the modified Hart method and the present provisional method, mixtures of a neutral fat and fatty acid were prepared whose total fat and neutral fat content would be known. The neutral fat used was cold pressed menhaden fish oil and the fatty acid was purified, commercial oleic acid. Two mixtures were prepared and sent to the committee marked as samples No. 4 & 5. Sample No. 4 was made of 25% menhaden fish oil and 75% oleic acid and after correcting for the free fatty acid in the fish oil, contained 24.27% neutral fat. Sample No. 5 was made with the same proportions reversed so that after correcting it contained 72.10% neutral fat.

The instructions sent with these samples were as follows:—

METHOD A.

Saponification Value of Fat.—About 10 grams of sample is boiled with 60 cc. of HCl (1:15) for 40 minutes (use glass beads to prevent bumping); transfer to a separatory funnel, extract the fat with ethyl ether, and wash until free from mineral acid, using salt solution to effect sharp separation and finally with water. Evaporate and dry ether extract, filter about 3 grams into a tared Erlenmeyer and weigh accurately. Add 25 cc. of approximately normal alcoholic KOH, boil under reflux for 30 minutes and titrate excess of alkali with N/2 H_2SO_4 using phenolphthalein as indicator. Calculate difference, between N/2 H_2SO_4 value of the alcoholic potash used and the number of cc. N/2 H_2SO_4 used for excess of alkali, to mmg. KOH per gram = E.

Saponification Value of Sample.—Weigh from 3 to 4 grams of sample into an Erlenmeyer, add 25 cc. of approximately normal alcoholic KOH and boil 30 minutes under reflux. Titrate excess alkali with N/2 H_2SO_4 and calculate to mmg. KOH per gram = D.

Free fatty acids.—Weigh 8 grams into beaker, add 50 cc. 95% alcohol and run in N/2 NaOH to end point with phenolphthalein. Boil gently for 20 minutes and add N/2 NaOH again to end point. Add 150 cc. water and 5 cc. methyl orange and titrate to acid end point with N/2 H_2SO_4. Number cc. of N/2 H_2SO_4 required, calculating to mmg. KOH per gram is equivalent to the combined and free fatty acids = B.

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Calculation from above results:

$$\text{Per cent. total fatty matter} = \frac{D \times 100}{E}$$

$$\text{Per cent. neutral fat} = \frac{(D - B)\ 100}{E}.$$

NOTES:—When running saponification value the alcoholic potash solution should be standardized for each group of determinations by running a blank test with the same quantity of alcoholic potash and under the same conditions as the sample.

All determinations are to be made in duplicate.

When reporting, give results of all determinations.

METHOD B.

Total Fatty Matter.—Weigh 4 grams into an Erlenmeyer and boil for 40 minutes with 30 cc. HCl (1:15) using glass beads to prevent bumping. Cool, transfer to a separatory funnel and extract fat with ethyl ether. Wash ethereal layer not less than three times with 75 cc. water using a little dilute HCl if necessary to break emulsions. Transfer to a tared beaker, evaporate, dry, cool and weigh.

Neutral Fat.—(1). Weigh 10 grams into an Erlenmeyer, add 50 cc. alcohol, boil under reflux 5 minutes and titrate with N/1 NaOH till slightly alkaline (using phenolphthalein). Transfer to a separatory funnel and extract with petroleum ether at least three times using 50 cc. for each extraction. Wash ether extracts at least three times, first with 50% alcohol and finally with distilled water. Transfer petroleum ether extract to tared beaker, evaporate, dry, cool and weigh.

(2). 10 grams of sample dissolved in mixture of 50 cc. water, 20 cc. ammonia and 30 cc. glycerine. Transfer to separatory with 150 cc. of ethyl ether and 15 cc. of alcohol. Shake until good foaming emulsion results and allow to separate. Extract soap solution twice again with 100 cc. ether. The combined ether extracts are washed with 20 cc. water then with 20 cc. dilute HCl and twice again with water. Transfer to a tared beaker, evaporate, dry and weigh. Determine free fatty acids in residue, calculate to oleic and deduct from residue.

The results obtained according to these instructions are given in Table III, and Table IV gives the original results of the com-

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mittee from which the final results by method A, given in Table III, were calculated. It will be seen that the determinations by both methods give results that only approximate the correct values and that for the mixtures used method A is slightly better than method B. From Table IV it can be seen that after boiling the fat with dilute HCl, extracting with ether, evaporating and drying, the saponification value is consistently higher in every case. This fact makes the results for total fat and neutral fat lower than they should be, and as it is, the results are already too high. The sources of the errors that give the higher results lie in the free fatty acid determination and in using the mean molecular weight or rather the mean saponification value as the value of the neutral fat. The latter causes the greatest error as can be seen from the mixtures used for this committee work. The saponification values of the fish oil and oleic acid were found to be 195.1 and 186.7 respectively while for a 25-75% mixture as in sample No. 4 the average would be 188.8. Hence if 188.8 is used in place of 195.1 we cannot expect otherwise than to obtain higher results. Perhaps the case in hand is unusual and differs from a sulphonated oil where the molecular weight of the fatty acids would be lower than that of the neutral fat but nevertheless we would have the error but in a different direction, that is, the result for neutral fat would be too low.

It has been noted above that the saponification value of the fat was higher than that of the sample and it seems from subsequent tests that this is caused by heating, simultaneous with a loss in weight. Neither of the samples contained even traces of water nor did the original oils from which they were made. An evaporation test, however, gave the following results:

	Fatty acids loss per cent.	Fish oil gain per cent.	Sample 4 loss per cent.	Sample 5 loss per cent.
1 hr. @ 100-105.....	2.26	0.44	1.51	0.20
2 hrs. " 100-105.....	3.81	0.52	2.73	0.56

A sample of the fatty acids heated for 6 hours at 100-110° C. gave a loss of 19.40% and a saponification value of 207.4. A similar sample of the fish oil heated for the same time and under the same conditions gave a loss of 0.50% and a saponification value of 231.4.

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TABLE III.

METHOD A.

Sample No. 4.	Cuthbert	Pierson	Hart and Liberthson	Faust & Fortner	Bumcke	Schultz	Average	Composition	Difference of average from composition
Total fatty matter	97.87	99.1	98.5	100.3	97.97	97.87	98.60	100.00	—1.40
Neutral fat	25.53	27.1	27.7	26.70	28.00	26.91	26.99	24.27	+2.72
Sample No. 5.									
Total fatty matter	97.50	97.7	98.6	98.90	98.13	99.33	98.27	100.00	—1.73
Neutral fat	75.96	70.5	76.9	76.90	76.70	77.33	75.72	72.10	+3.62

METHOD B.

Sample No. 4.									
Total fatty matter	98.06	98.4	96.6		99.26	98.14	98.09	100.00	—1.91
Neutral fat I.....	31.84	32.4	29.8		33.03	31.36	31.68	24.27	+7.41
Neutral fat II.....	27.03				35.47	33.29			
Sample No. 5.									
Total fatty matter	99.18	100.01	98.7	96.68	99.79	98.93	98.88	100.00	—1.12
Neutral fat I.....	78.98	71.20	77.8	76.94	80.10	79.52	77.42	72.10	+5.32
Neutral fat II.....	77.63				81.58	79.63			

Sample No. 4 is a mixture of 25% menhaden fish oil and 75% oleic acid.
Sample No. 5 is a mixture of 75% menhaden fish oil and 25% oleic acid.

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TABLE IV.

RESULT BY METHOD A FROM WHICH CALCULATIONS WERE MADE.

Sample No. 4.	Cuthbert	Pierson	Hart and Liberthson	Faust and Fortner	Bumcke	Schultz	Average	Greatest difference
Combined and free fatty acids—B...	137.3	134.8	137.5	138.8	134.7	136.6	136.6	4.1
Saponification value of sample—D...	185.8	185.0	191.3	189.5	188.6	189.8	188.3	6.3
Saponification value of fat—E.....	189.8	187.4	194.3	189.5	192.5	193.9	191.2	6.9
Sample No. 5.								
Combined and free fatty acids—B...	41.8	*52.4	42.5	43.7	42.0	42.8	42.6	1.9
Saponification value of sample—D...	189.0	188.9	192.5	193.7	193.3	194.1	191.9	5.2
Saponification value of fat—E.....	193.8	193.1	195.3	194.9	197.0	195.4	194.8	3.9

* Omitted from average.

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The low results for total fatty matter by method B may be explained by the loss due to heating when it is dried.

The committee was composed of the following members:—

C. G. Bumcke, National Oil Products Co., Harrison, N. J.
L. A. Cuthbert, Elk Tanning Co., Ridgway, Pa.
T. A. Faust, Yocum-Faust, Ltd., London, Canada.
Ralph Hart, Chemical Laboratories of New York, New York City.
H. L. Pierson, Waterbury Clock Co., Waterbury, Conn.
G. W. Schultz, Elk Tanning Co., Ridgway, Pa.
L. J. Vaudreuil, Graton & Knight Mfg. Co., Worcester, Mass.

Comments and Recommendations.

C. G. Bumcke: For the titration of total alkali and combined SO_3 I use 500 cc. Erlenmeyer flasks as the large amount of liquid can be shaken better in the bigger receptacle.

As in the determination of combined SO_3, I also used ether and salt solution to improve the titration of total alkali. I used a larger amount of ether than given in the instructions, about 50 cc. The method, as Mr. Hart himself admitted to me, was originally intended to be used for light oils only, like sulphonated castor, corn and rapeseed oils. When used with dark oils, like sulphonated cod oils, it has some difficulties, though it is much improved by the application of sulphuric ether and sufficient salt solution. It saves time, but requires practice which naturally would be lacking when such tests are only made occasionally.

For the determination of total SO_3 in method B, I used 25-30 cc. dil. hydrochloric acid 1:5. I washed the ethereal layer with water until free from mineral acid which is at least half a dozen times.

For the determination of SO_3 in salts I use 8-10 g. oil, 20-30 cc. conc. salt solution for the first and 10 cc. for the next three extractions. I do not filter the combined salt solutions but I dilute them with 4 to 5 times the volume of water before acidifying, boiling and precipitating with $BaCl_2$.

As to the salt solution used, I want to say that I always keep some salt on the bottom of my supply to insure as much concentration as possible. I consider it an unnecessary effort to use a 23% solution. As the salt solution of the first extraction is diluted by the water contained in the oil, it is of no use to strive for a certain concentration, in many cases "as concentrated as

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possible" is not concentrated enough for oils that contain 40-50% or more water. Such oils should be dried before, in order to prevent sulpho-fatty acids or their soaps from entering into the salt solution, as their own water content could so dilute the brine that these acids and their salts become soluble.

As to the testing of samples 4 and 5, I want to say that I do not apply such methods as are given in your instructions for oils that are neither sulphonated nor contain any soaps. For this reason I hesitated to make these tests at all as I considered them a rather unnecessary waste of time. Discrepancies in the results occur very easily where the material has to be dried in an oven, as time and temperature will always vary. For instance my lower results in determination No. 1 of Neutral Fat were caused by more heat (115° C.) and longer exposure to this heat than I intended. For exact results careful drying at comparatively low temperatures in a current of CO_2 is necessary.

For titrations of alcoholic soap solutions for the determination of the saponification value, I always use N/2 hydrochloric acid as KCl is soluble, while K_2SO_4 is insoluble in the dil. alcoholic solution.

The determination of the free fatty acids is better done in a 500 cc. Erlenmeyer than in a beaker.

The saponification value is determined with 2-2.5 g. oil and 25 cc. N/2 alcoholic KOH.

In method B, neutral fat No. 1 the dilution of the alcohol to about 50% for the petrol ether extraction was omitted.

R. HART: In making total alkali and combined SO_3 determinations 30 grams of granulated salt and 25 cc. of ether were added, 5 cc. of 0.04% of methyl orange were used as an indicator.

By disregarding those results in your report for the combined SO_3, which vary by more than 5% from the average, the maximum differences in per cent. among the various analyses are as follows:

	Sample No. 1	Sample No. 2	Sample No. 3	Average
Method A	0.27	0.16	0.20	0.21
Method B	0.11	0.22	0.13	0.15

The chance for agreement between different analysts, is, therefore, slightly in favor of method B. However, most of the men

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have probably had considerably more experience with this method than with method A, hence, more familiarity with method A should yield the more concordant results.

By rejecting part of the data as above, the average combined SO_3 for sample No. 3 by method B becomes 3.03%. Referring now to Table II, it will be noticed that method A gave in all three cases 0.12% lower results than by method B. It is, of course, difficult to state which of the methods is the more correct, but the saving of time and ease of manipulation are decidedly in favor of method A for the determination of combined SO_3.

Personally I believe that the determination of total fat by method A is more accurate than by the usual gravimetric method. Consider, for example, the following: Suppose a mixture of 80% corn oil fatty acids, saponification value 200, and 20% of a volatile fatty acid, saponification value 300, be heated to constant weight or until the volatile fatty acids are completely vaporized. The saponification value of the heated oil would be 200 while the correct figure is 220, or an error of 10% in the fat determination. The direct method, on the other hand, would show a loss of 20%.

A valuable modification of this method would be in deciding on a constant for the saponification value of the extracted, decomposed cod oil. Total fat could then be determined very rapidly and exactly and the elements of variation in the analysis by different chemists would be reduced to a minimum.

L. A. CUTHBERT: In my opinion the results as obtained by various members of this committee agree very well. Closer agreement in the analysis of any oil than that shown by the results obtained for samples 1, 2 & 3 under method B cannot be expected. The results for these samples obtained under method A do not agree as well; this, however, is no doubt due to the fact that members of the committee were not as familiar with the method. The exact end point in the titrations is sometimes difficult to see and for this reason determinations by various chemists would probably not show as uniform results as determinations made by the gravimetric method. Greater familiarity with method A would no doubt eliminate some of the error.

It will be noticed, however, that the percentages of Combined SO_3 under method A are in almost every case lower than those obtained under method B. In a similar manner the results for

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Combined SO_3 obtained under method B are usually somewhat lower than the results obtained by ashing the oil with Na_2CO_3 and determining the SO_3 gravimetrically as suggested by W. K. Alsop a few years ago. In my opinion the latter method gives the most accurate results for SO_3 in a sulphonated oil. For this reason I do not believe that method A should be made the official method; though, due to the fact that it is a rapid and easy method to carry out, I would favor making it a provisional method.

The determinations of total fatty matter in samples 4 and 5 under both methods give results which are fairly uniform. In my own determinations method A gives results slightly lower than method B and offers no advantages as far as manipulation is concerned.

It is the opinion of the chairman that a difference of 1% more or less from the actual content of total fatty matter and a difference of 2% more or less for neutral fat is not very material in the valuation of a sulphonated oil and therefore would recommend that total fatty matter in a pure oil be determined as the difference between 100 and the sum of moisture, ash, unsaponifiable, ammonia and combined SO_3. From the saponification value of the sample and this value for total fat, the saponification value of the fat can be calculated and this value may be used to calculate the neutral fat after deducting the value for combined and free fatty acid from the saponification value of the sample.

The chairman recommends that the analysis of sulphonated oils contain the following determinations:

(1) Moisture, Ash, Unsaponifiable, Combined SO_3, Ammonia and Total Fatty Matter.

(2) Total Alkali and Free Fatty Acids (expressed in milligrams of KOH per gram) and Neutral Fat (optional). The chairman suggests that the following procedures be recommended for adoption as official methods of the Association:

Moisture.—The Xylol method as given in the provisional methods and as alternative the method as recommended by the committee for 1917, this JOUR. **12**, 276 (1917).

Ash.—The determination as given in the provisional methods.

Unsaponifiable.—The method as given in the committee report for 1919 under method B, this JOUR. **14**, 268 (1919).

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Combined SO_3 and Total Alkali.—As given in this report under method A, page 283, however, making the total alkali determination read: Weigh 10 grams into a 250 cc. Erlenmeyer, dissolve in 150 cc. water (warm if necessary to effect solution), add 30 grams granulated salt, 25 cc. ether and 5 cc. of methyl orange indicator and titrate with N/2 H_2SO_4. The method for combined SO_3 as given under method B be adopted as alternate method.

Ammonia and Free Fatty Acids.—As given under method A in the 1919 committee report, this JOUR. **14**, 267 (1919).

Total Fatty Matter.—To be taken as the difference between 100 and the sum of moisture, ash, unsaponifiable, ammonia and combined SO_3 as determined above.

Neutral Fat.—Determine the saponification value of the sample as given in this report, page 286, and calculate to sap. val. of fat by dividing by the weight of total fatty matter. From the sap. val. of the sample subtract the combined values of total alkali and free fatty acids and divide the remainder by the sap. val. of fat. This result multiplied by 100 is equal to the per cent. of neutral fat.

THE TRUE TANNING VALUE OF VEGETABLE TANNING MATERIALS.[1]

By John Arthur Wilson and Erwin J. Kern.

During the past century an enormous amount of energy has been expended in efforts to devise a method for determining the tannin content, or rather the true tanning value, of vegetable materials. Numerous methods have been proposed,[2] but without any indication as to the correctness of the results obtained. In fact the methods now in general use, both here and in Europe, were made official without any knowledge as to their accuracy, but solely because they are of such nature that different analysts have comparatively little difficulty in getting concordant results. Since tanning materials are usually sold on a tannin basis, these

[1] Presented to the Section of Leather Chemistry at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 14, 1920. Reprinted from *J. E. & I. C.*, May, 1920.

[2] For a review of work done since 1803, see Procter's "Leather Industries' Laboratory Book" (Spon, 1908), pp. 168-176.

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methods have proved of very great value in enabling buyer and seller to agree as to price, but investigators who have blindly accepted the results as reliable have sometimes been led into serious error. In this paper we present what we believe to be the first successful method for determining the true tanning value of vegetable materials.

PRACTICAL DEFINITION OF TANNIN

Work on the chemistry of the tannins is still so far from complete that no rigid chemical definition of them as a class can be given, but their extensive use, especially in the leather industry, has necessitated defining them in terms of some property of practical value. It has therefore become customary to apply the name *tannin* to that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fiber which are resistant to washing. The remaining portion of the soluble matter is called *non-tannin*.

NEW METHOD

Principle of the Method.—The method aims, of course, to determine exactly what is called for in the definition. A convenient amount of the tanning material is shaken with a definite amount of purified hide powder until all tannin has been removed from solution. This point is determined by filtering off a portion of the residual liquor and adding drop by drop, avoiding a large excess, a solution containing 10 g. of gelatin and 100 g. of sodium chloride per liter; if the solution becomes turbid or a precipitate forms, it shows that all tannin has not been removed from solution, in which case the mixture must be discarded and the test repeated, using less of the tanning material or shaking for a longer time, until the solution after filtration gives no visible reaction with the gelatin-salt reagent. The tanned powder is then washed free from soluble matter, including the non-tannin removed from solution by the hide powder, which is responsible for the large errors in the methods now in use. It is then carefully dried and analyzed for tannin as in the regular procedure for vegetable-tanned leathers, and from this figure the percentage of tannin in the original material may readily be calculated.

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Sensitivity of Gelatin-Salt Test and its Effect Upon the Method.—The gelatin-salt test appears to be the most satisfactory one known for determining whether or not a tan liquor has been completely detannized. In the present official methods, it is assumed that the hide powder completely detannizes the liquor because the non-tannin filtrate remains clear upon addition of the gelatin-salt reagent. This reagent, however, gives negative results with extremely dilute solutions of tannin. Another fact tending to make it difficult to detect the presence of small amounts of free tannin in the liquor after shaking with hide powder is that these liquors are always turbid and must be filtered, and it is a known fact that filter paper will remove tannin from solution to some extent. It was therefore essential to determine the sensitivity of the test for the conditions under which the analyses were made.

If the time of shaking, volume of tan liquor, and quantity of hide powder are kept constant, the less the concentration of the liquor the greater will be the fraction of tannin removed by the hide powder. This made it desirable in checking the accuracy of the work to make several sets of analyses for each tanning material examined, using a different concentration of liquor in each case. The most concentrated solution of each material noted in Table I was used to test the sensitivity of the gelatin-salt reagent by diluting to greater and greater extent and *then* filtering and testing with the reagent under the same conditions as employed in the actual analyses. The reagent was added a drop at a time to 10 cc. of the clear filtrate in a test tube. The dilutions at which the test failed, expressed in cc. of tan liquor diluted to 100 cc., were as follows: quebracho 1, hemlock bark 2, oak bark 2, larch bark 2, chestnut wood 0.5, osage orange 2, sumac 1, and gambier 4. It therefore follows, since the detannized filtrates from all these liquors gave a negative test with the gelatin-salt reagent, that more than 95 per cent. of the tannin of the gambier liquor and more than 97 per cent. of the tannin of every other liquor were removed from solution by the hide powder. But, the analyses were also carried out with much more dilute liquors, from which the hide powder should remove an even greater percentage of the tannin. Since the results obtained for any one material, using several dilutions, checked so closely, we may

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reasonably conclude that the hide powder removed *practically* all of the tannin from all solutions which gave no test with the gelatin-salt reagent after the shaking process.

Hide Powder.—The hide powder used in this work is a highly purified product known as American Standard and is prepared by the Standard Mfg. Co. of Ridgway, Pa., especially for use in the analysis of tanning materials. Since this hide powder is of variable composition due to changes in water content, it was necessary to base our calculations upon the protein it contained, to which we shall hereafter refer simply as hide substance. Von Schroeder[1] found hide substance to contain 17.8 per cent. of nitrogen, which figure is generally accepted. The per cent. of nitrogen determined by the Kjeldahl method, multiplied by 5.62 should therefore give the per cent. of hide substance. The hide powder used in this work showed by analysis

	Per cent.
Water	12.29
Ash	0.36
Fat (chloroform extract)	0.82
Hide substance (N × 5.62)	86.50
Total	99.97

from which it would appear that the factor 5.62 is correct.

Materials Examined.—Eight materials were selected for examination which are fairly extensively used and which show great differences in properties, especially in so-called astringency. The solid quebracho extract and the four liquid extracts of oak bark, larch bark, chestnut wood, and osage orange are typical samples of the best of these materials now on the American market. The gambier is the ordinary pasty product from the East Indies; the sumac, consisting of ground leaves and small twigs, is from a reputable dealer in Palermo; and the hemlock bark came from the forests of Wisconsin.

Procedure.—The extracts were simply dissolved in hot water, cooled slowly, and made up to the mark. The bark and sumac were finely ground and leached by percolation, only the extracted portions being used after making up to definite volume. In each test, 12 g. of hide powder (of known hide substance content) were put into a wide-mouth, rubber-stoppered, half-pint bottle,

[1] Procter, *Loc. cit.*

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the tanning material dissolved in 200 cc. of solution was added, and the whole was shaken in a rotating box for 6 hrs.

The amount of material that could be used was limited by the amount of tannin that the hide powder was capable of taking up in 6 hrs. On the other hand it was desirable not to use too little, since the less the amount of tannin fixed per unit of hide substance, the less the accuracy of the method since the tannin was determined by difference. Whenever the liquor after the 6-hr. shaking gave a turbidity or precipitate with the gelatin-salt reagent, the test was repeated with less material. The smallest amount used for any material represents the least we were able to use and still get reproducible results.

The tanned powder was washed by shaking with 200 cc. of water for 30 min., squeezing through a suitable cloth, and repeating the washing operation until the wash water showed no color and gave no test with ferric chloride solution. Except for the osage orange and chestnut wood extracts, which are unusual in several respects, not more than 12 washings were required to free the powders from non-tannin, which shows that the line of demarcation between tannin and non-tannin is fairly sharp for the commoner materials. The wash water continued to extract coloring matter from the powders tanned with osage orange until after the fiftieth washing, while as many as 25 washings were required to free the powders tanned with chestnut wood from soluble matter producing a dark color with ferric chloride. All wash water was tested with the gelatin-salt reagent, but in every case the test was negative. This method of washing was found to be more efficient than using running water on a suction filter, probably because the mechanical agitation assists the diffusion of soluble matter from the interior of the hide fibers.

The washed powders were dried at room temperature for 24 hrs. or longer and then analyzed for water, ash, fat, and hide substance. The difference between 100 and the sum of these percentages was taken as the per cent. of tannin in the leather. The parts of tannin per 100 parts of hide substance in the leather divided by parts of tanning material used per 100 parts of hide substance give the fraction of tannin in the original material.

The results for the 8 materials examined are given in Table I.

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TABLE I.

Material	Material Grams per liter	Percentage Analysis of Tanned Hide Powder					Per 100 G. of Hide substance		Tannin in material Per cent.
		Water	Ash	Fat	Hide substance (N × 5.62)	Tannin (by difference)	Tannin found Grams	Material used Grams	
Quebracho	18.8	11.56	0.14	0.35	74.92	13.03	17.39	36.8	47.26
Quebracho	18.8	11.42	0.08	0.35	75.05	13.10	17.46	36.8	47.45
Quebracho	11.5	13.81	0.03	0.30	77.53	8.33	10.74	22.6	47.52
Hemlock Bark	150.0	9.94	0.12	0.24	76.54	13.16	17.19	287.9	5.97
Hemlock Bark	100.0	10.73	0.13	0.28	79.39	9.47	11.93	191.9	6.22
Hemlock Bark	75.0	12.76	0.05	0.28	79.53	7.38	9.28	147.1	6.31
Oak Bark	67.5	12.54	0.07	0.12	74.76	12.51	16.73	131.6	12.71
Oak Bark	45.0	11.19	0.09	0.24	79.36	9.12	11.49	87.6	13.12
Oak Bark	25.0	13.53	0.05	0.34	81.00	5.08	6.27	48.9	12.82
Larch Bark	67.5	12.59	0.09	0.13	75.61	11.58	15.32	131.6	11.64
Larch Bark	45.0	13.65	0.09	0.30	77.90	8.06	10.35	87.7	11.80
Larch Bark	25.0	16.52	0.08	0.25	78.65	4.50	5.72	48.9	11.70
Chestnut Wood	67.5	12.43	0.11	0.05	75.76	11.65	15.38	131.6	11.69
Chestnut Wood	45.0	12.82	0.13	0.19	78.54	8.32	10.59	87.7	12.08
Chestnut Wood	37.5	12.05	0.10	0.21	80.74	6.90	8.55	71.7	11.92
Sumac	93.8	11.39	0.16	0.36	74.92	13.17	17.58	179.3	9.80
Sumac	62.5	12.26	0.23	0.31	78.38	8.82	11.25	119.5	9.41
Sumac	37.5	11.75	0.12	0.37	81.97	5.79	7.06	73.5	9.61
Osage Orange	48.8	12.82	0.13	0.17	77.35	9.53	12.32	95.0	12.97
Osage Orange	32.5	12.83	0.09	0.25	80.09	6.74	8.42	63.3	13.30
Osage Orange	26.3	12.43	0.12	0.25	81.43	5.77	7.09	51.2	13.85
Gambier	50.0	12.08	0.18	0.19	81.44	6.11	7.50	97.4	7.70
Gambier	49.5	11.77	0.26	0.28	81.70	5.99	7.33	94.7	7.74
Gambier	29.0	13.06	0.14	0.35	82.74	3.71	4.48	56.5	7.93

COMPARISON WITH A. L. C. A. METHOD

Practically all tanning materials are bought and sold in this country on the basis of tannin content as determined by the official method of the American Leather Chemists Association. The principle of the method is similar to that of the new method as regards the shaking of a solution of the tanning material with hide powder, but differs in that the drop in concentration of the liquor upon shaking is taken as the measure of its tannin content, while the tanned powder is simply discarded. The details of the A. L. C. A.[1] method follow:

The hide powder is specially prepared by giving it a light chrome tannage with chrome alum, washing it practically free from soluble matter, and squeezing it until it contains not less than 71 nor more than 74 per

[1] This JOUR., 14, (1919), 654.

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cent. of water. The solution of tanning material for analysis must contain not less than 0.375 nor more than 0.425 g. of tannin per 100 cc., as found by this method. To 200 cc. of this solution is added such an amount of the wet hide powder as contains not less than 12.2 nor more than 12.8 g. dry hide powder and the whole is shaken for 10 min. The limits defined are to some extent arbitrary, but it has been found necessary to set limits of some sort in order to get concordant results. The detannized solution is separated from the powder by squeezing through linen and is then filtered through paper, after the addition of kaolin, the solution being returned until the filtrate is quite clear. The amount of residue from an aliquot portion of this filtrate, after correcting for the water introduced by the hide powder, is taken as a measure of the non-tannin in the original material. The difference between the total soluble matter and the non-tannin is called tannin.

Several outstanding sources of error in this method were emphasized by the authors in an earlier paper.[1] The most serious defect is that it does not take into account the fact that hide powder removes non-tannin of certain kinds, such as gallic acid pyrocatechol, etc., from solution to an extent depending upon the concentration . These substances do not make leather and are readily washed out. This explains the fact that where tanners try to keep a rigid cost account of tanning materials, they find no such amount of tannin in the leather as would be expected from the amount of tannin used, as determined by the A. L. C. A. method. The analyses of the 8 materials by the A. L. C. A. method are given in Table II along with a calculation of the percentage errors involved in this method, made upon the assumption that the results obtained by the new method are correct.

TABLE II.

	Percentage Analysis of Material — A. L. C. A. Method					
			Soluble matter			
Material	Water	Insoluble matter	Non-tannin	Tannin	New method tannin	Percentage error in A. L. C. A. method
Quebracho	17.87	7.16	6.96	68.01	47.41	43
Hemlock Bark	8.90	74.33	6.71	10.06	6.17	63
Oak Bark	52.66	3.68	19.46	24.20	12.88	88
Larch Bark	51.08	5.88	20.90	22.14	11.71	89
Chestnut Wood	58.90	1.50	13.80	25.80	11.90	117
Sumac	9.25	47.20	17.99	25.56	9.61	166
Osage Orange	46.05	3.45	10.63	39.87	13.37	198
Gambier	51.12	5.36	18.57	24.95	7.79	220

[1] This JOUR., 13, (1918), 429.

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Although the enormous errors in the A. L. C. A. method are nothing short of sensational, we are convinced that they are not at all exaggerated. The extent of these errors is less surprizing, however, when the behavior of certain non-tannins, like gallic acid, in the presence of hide powder is studied. A series of solutions of gallic acid of different strengths were prepared and treated by the A. L. C. A. method as though they were tan liquors of the required strength. The results for non-tannin should have been 100 per cent. in every case, if the method were reliable, but the actual data in Table III show that a very large proportion

TABLE III.—RESULTS OF TREATMENT OF PURE GALLIC ACID SOLUTIONS BY THE A. L. C. A. METHOD, USING 47 G. OF WET HIDE POWDER (73% WATER) TO 200 CC. OF SOLUTION.

Gallic Acid Grams per Liter	Non-tannin Per cent.	Tannin Per cent.
8.88	54.0	46.0
4.44	47.1	52.9
2.22	43.8	56.2
1.11	40.4	59.6

TABLE IV.—EFFECT OF ALTERING THE PROPORTION OF HIDE POWDER UPON THE AMOUNT OF GALLIC ACID REMOVED BY THE HIDE POWDER FROM AN 0.888 PER CENT. SOLUTION, USING THE PRINCIPLE OF THE A. L. C. A. METHOD.

Wet Hide Powder (73% water) G. per 200 cc.	Non-tannin Per cent.	Tannin Per cent.
5	91.8	8.2
10	86.0	14.0
25	69.6	30.4
50	52.1	47.9
75	43.7	56.3

of the acid is taken up by the hide powder. Table IV shows that the amount of gallic acid removed from solution is very largely dependent upon the proportion of hide powder employed. Our results by the new method for gambier indicate that this sample contains more than 4 times as much non-tannin as tannin. When we consider that more than 50 per cent. of these non-tannins may be removed from solution by the hide powder, errors exceeding 200 per cent. are to be expected by the A. L. C. A. method.

The reason for the necessity of arbitrary limits in the official method is suggested by the gallic acid experiments, but is more strongly emphasized by similar experiments upon actual tan liquors. The effect of altering the proportion of hide powder with

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solutions of the 8 tanning materials is shown in Table V and Figs. 1 and 1*a*. The zero points in the figure represent the percentages of tannin found by the new method. In none of these

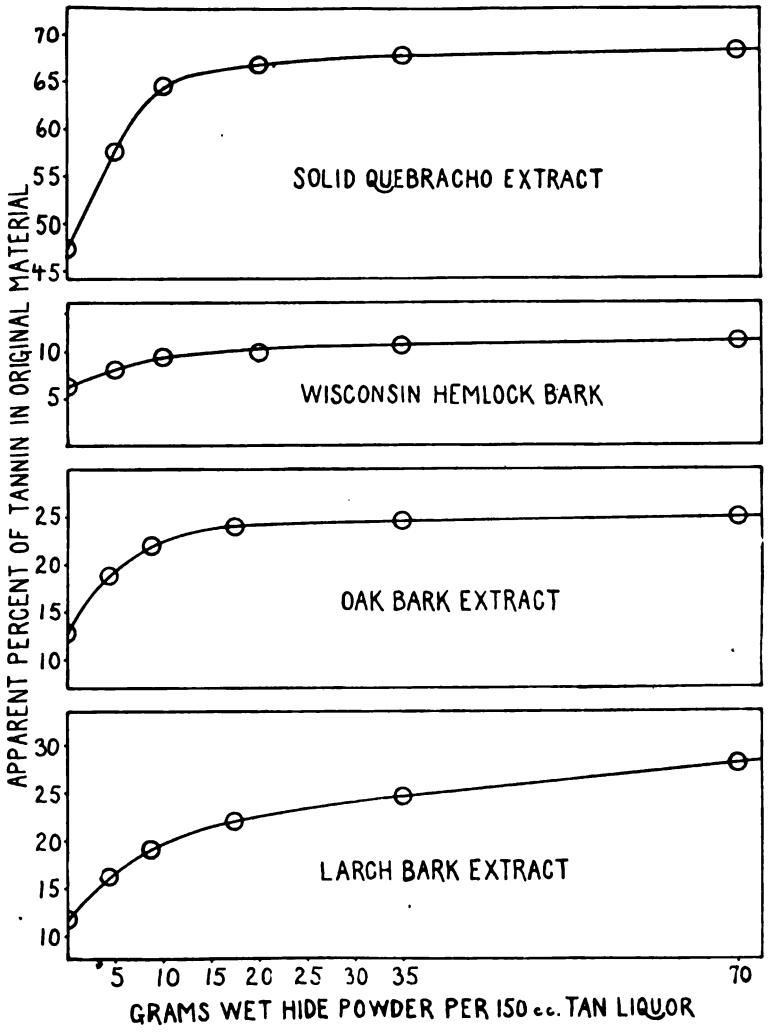

Fig. 1.

experiments did the solution after shaking give a test with the gelatin-salt reagent, but we nevertheless find enormous increases in per cent. of tannin due to increasing the proportion of hide

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powder. This alone should be sufficient to show that the A. L. C. A. method can not be considered an exact one and that the arbitrary limits were set so that different analysts would get concordant rather than more nearly correct results. Table V and Fig. 2 show how the percentage error inceases with increasing proportions of hide powder.

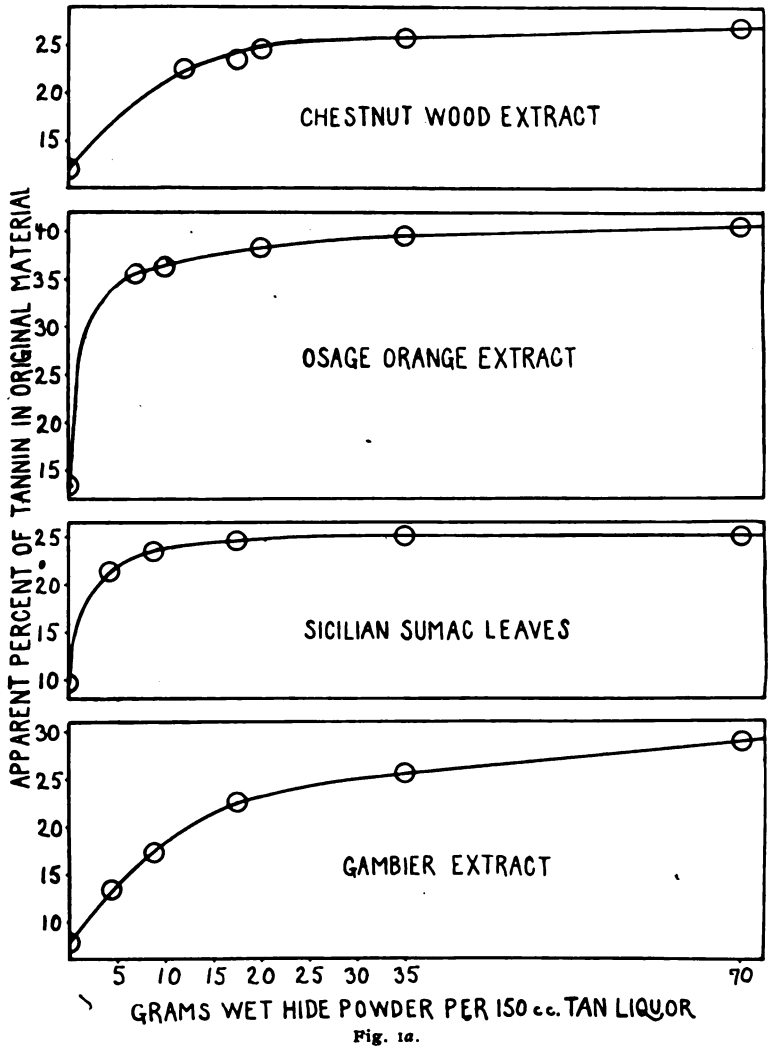

Fig. 1a.

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TABLE V.

Material	Grams per liter	Wet hide powder (73% water) used to detannize 150 cc. tan liquor. Grams	Apparent per cent. of tannin	Percentage error due to hide powder
Quebracho	3	70.0	68.18	44
		35.0	67.56	43
		20.0	66.61	40
		10.0	64.36	36
		5.0	57.56	21
Hemlock Bark	20	70.0	10.98	78
		35.0	10.60	72
		20.0	9.76	58
		10.0	9.35	52
		5.0	7.98	29
Oak Bark	4.11	70.0	25.02	94
		35.0	24.59	91
		17.5	24.01	86
		8.8	22.09	72
		4.4	18.77	46
Larch Bark	4.37	70.0	28.10	140
		35.0	24.52	109
		17.5	21.97	88
		8.8	19.10	63
		4.4	16.24	39
Chestnut Wood	15	70.0	26.87	126
		35.0	25.80	117
		20.0	24.59	107
		17.5	23.52	98
		12.0	22.49	89
Sumac	4	70.0	24.98	160
		35.0	25.05	161
		17.5	24.47	155
		8.8	23.45	144
		4.4	21.45	123
Osage Orange	8	70.0	40.48	203
		35.0	39.47	195
		20.0	38.21	186
		10.0	36.27	171
		7.0	35.67	167
Gambier	4.58	70.0	29.04	273
		35.0	25.60	229
		17.5	22.56	190
		8.8	17.22	121
		4.4	13.38	72

As might be expected, the greatest errors in the official method are obtained with those materials containing the greatest propor-

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tion of non-tannin to tannin. Quebracho, having least non-tannin, gives the smallest error. However, if the quebracho is mixed with gallic acid to make the proportion of non-tannin to tannin

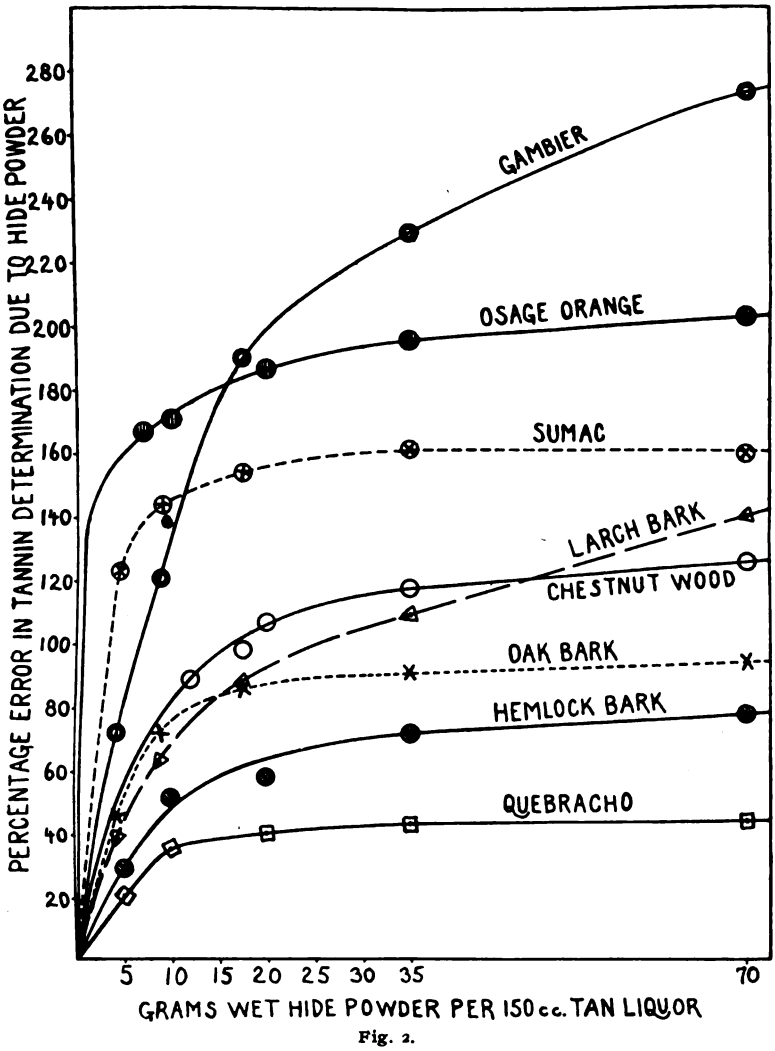

Fig. 2.

about the same as in the case of the gambier, it gives errors nearly as great as in the case of the gambier. This is shown in Table VI.

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TABLE VI.

Wet hide powder (73% water) used to detannize 150 cc. tan liquor Grams	Percentage analysis of mixture of 5 parts of quebracho extract to 9 parts of dry gallic acid					Percentage error due to hide powder		
	A. L. C. A. Method					Quebracho		
			Soluble matter					
	Water	Insoluble matter	Non-tannin	Tannin	New method Tannin	Alone (from Fig. II)	In presence of Gallic acid	Gambier (from Table V)
4.4	5.80	3.96	63.34	26.90	16.93	18	59	72
8.8	5.80	3.96	53.39	36.85	16.93	33	118	121
17.5	5.80	3.96	44.07	46.17	16.93	39	173	190
35.0	5.80	3.96	37.14	53.10	16.93	43	214	229
70.0	5.80	3.96	33.87	56.37	16.93	44	233	273

Comparison of the two methods has brought out at least one fact of practical significance: Those materials which give the least errors are most astringent, while those giving greatest errors are least astringent. The order of the materials in Table II might almost be taken as the order of decreasing astringency, although an exact parallelism can not be claimed since we have no quantitative measure of astringency. Quebracho and hemlock bark are generally conceded to be the most astringent, and sumac and gambier the least astringent of these materials. This suggested a relation between astringency and the ratio of non-tannin to tannin. In the experiments listed in Table I, the hide powder fixed more than twice as much tannin from the quebracho liquors in 3 hrs. as from the gambier liquors in 6 hrs. But, when enough gallic acid was added to the stronger quebracho liquors to give them the same proportion of non-tannin to tannin as in the gambier, the hide powder did not remove anywhere nearly all the tannin in 6 hrs. Upon addition of the gelatin-salt reagent to the liquors after shaking, huge precipitates were formed, suggesting a great reduction in astringency. That the effect was only one of slowing up the tanning action was proved by the fact that the hide powder was able to detannize the solution completely in 24 hrs.

PRACTICABILITY OF THE NEW METHOD

The new method in its present form requires more time than the A. L. C. A. method, but this disadvantage must be considered negligible compared to the advantage of greatly increased accuracy. If the new method is to prove satisfactory from the standpoint of setting a price on tanning materials, it must give results which are readily reproducible in different laboratories. We are

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convinced that it will do this quite as well as the official method when the different analysts become used to manipulating it. The several results for any one material in Table I were determined days, and sometimes weeks, apart. The hide powder used in the new method is not chromed, but is used exactly as it comes from the manufacturer. If, however, it is first chromed, it gives a higher result for osage orange, apparently due to the chrome acting as a mordant for the coloring matter. But this coloring matter does not precipitate gelatin nor does it form a stable compound with unchromed hide fiber and we feel that the method is the more accurate for not estimating this coloring matter as tannin. The question of putting a value on this coloring matter may have to be solved, but this problem will probably be confined to very few materials. On the whole we believe the new method will be found quite as practicable and certainly very much more satisfactory from the standpoint of accuracy than the present official method. What has been said concerning the A. L. C. A. method applies equally well to the European methods since they differ only in detail.

SUMMARY

A new method of tannin analysis is described which we believe determines exactly what is called for in the generally accepted definition of tannin from a practical viewpoint, namely, that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fiber which are resistant to washing.

The analyses of 8 common tanning materials by the new method and by the official method of the American Leather Chemists Association indicate that the latter method is in error to the extent of from 43 to 220 per cent.

The new method gives reproducible results and is considered entirely practicable.

COMMITTEE ON LIMEYARD CONTROL, I. THE ANALYSIS OF LIME LIQUORS.*

By Donald Burton.

The lack of co-ordination of the various original papers on lime-liquors suggested that a resumé of the present extent of our

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knowledge might be of interest to members of the Society and in particular serve as a foundation for further research.

The following are the principal references to the modes of action, and methods of analysis, of lime-liquors (papers dealing with special points being quoted in the text) :—

1. The Nature of the Liming Process. E. Stiasny. Translated from *Der Gerber*, 1906, by G. E. Knowles. *J. S. L. T. C.*, 1919, 129.
2. Recent Advances in the Bacteriology of Putrefaction. J. T. Wood, *Coll.*, 1906, 229-232, 236-239.
3. Mode of Action of Liming in Leather Manufacture. E. Stiasny, *Coll.*, 1907, 126.
4. The Amount of Skin Substance Dissolved in Fellmongers' Collecting Limes. J. T. Wood and S. R. Trotman, *Coll.*, 1910, 105. This JOUR. **5**, 272 (1910).
5. The Direct Estimation of Hide-Substance Dissolved in Lime and Tan Liquors. R. A. Earp, *Coll.*, 1907, 412. This JOUR., **3**, 63 (1908).
6. L'épilage à l'acide sulfureux. Urbain J. Thuau, *Coll.*, 1908, 362.
7. Eine rasche Bestimmung gelöster Hautsubstanz in Weichen und Aeschern. E. Stiasny, *Coll.*, 1908, 371. This JOUR. **3**, 398 (1908).
8. Bakterien in der Lederindustries. H. Becker, *Coll.*, 1909, 169.
9. Commercial Control of Tannery Lime-Liquors. H. G. Bennett, *Coll.*, 1909, 194. This JOUR. **4**, 143 (1909).
10. A Method for the Estimation of Nitrogen in Organic Substances; and in Particular, for the Determination of Hide-substance in Leathers and of Dissolved Hide-substance in the Soak Liquors and Lime Liquors of the Leather Factory. H. G. Bennett, *Coll.*, 1909, 197. This JOUR. **4**, 140 (1909).
11. An Explanation of the Causes which Conduce to "Looseness" or "Slackness" in Sheep Skins. Alfred Seymour-Jones, *Coll.*, 1909, 258-261, 265-268, 403-405, 409-411.
12. The Principles of Liming. R. W. Griffith. This JOUR. **5**, 109 (1910).
13. On Old Limes. E. Stiasny, *Coll.*, 1910, 181. This JOUR. **5**, 345 (1910).
14. Sensibilité de la peau verte, et de la peau après l'échauffe, les pelains, et les confits à l'egard de la chaux, du sel, et de l'acide acétique. G. Abt et E. Stiasny, *Coll.*, 1910, 189-199, 205-212.
15. The Bacteriology of the Leather Industry. J. T. Wood, *Coll.*, 1910, 384-388, 391-406. This JOUR. **5**, 630 (1910) and **6**, 249 (1911).
16. The Process of Liming. E. Andreis. This JOUR. **7**, 609 (1912).
17. Preliminary Report on Light Leather Liming Control. J. T. Wood and D. J. Law, *Coll.*, 1912, 121-130, 577. This JOUR. **7**, 346 (1912).

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18. The Liming Problem. A. Seymour-Jones, H. R. Procter, *Coll.*, 1913, 14.
19. Provisional Method of Analysis of Lime Liquors. *Coll.*, 1913, 73.
20. Depilatories an d their Influence upon Hides. R. W. Griffith. This Jour. **8**, 224 (1913).
21. Unhairing and Liming. W. Eitner. This Jour. **8**, 482 (1913).
22. Graphical Method of Recording Results. J. R. Blockey, *Coll.*, 1913, 628. This Jour. **8**, 383 (1913).
23. Notes on Depilating. A. Rogers. This Jour. **9**, 42 (1914).
24. Light Leather Liming Control. J. T. Wood, *Coll.*, 1914, 305.
25. The Analysis of Materials used in connection with Beam-House Procedure; Committee Report. C. R. Oberfell. This Jour. **10**, 252 (1915).
26. Chemical Control of the Beam-House. J. Helfrich. This Jour. **10**, 396 (1915).
27. The Analysis of Tannery Lime-Liquors. H. G. Bennett, *Coll.* (Lond.), 1915, 258-266, 313-322, 329-335. This Jour. **11**, 98 (1916).
28. A Study of the Changes in Skins during their Conversion into Leather. A. A. Schlichte. This Jour. **10**, 526-558, 585-612 (1915), *Coll.* (Lond.), 1916, 20-46, 61-77.
29. Fellmongering and Tanning Sheep-skins in New South Wales. F. A. Coombs, E. Swinbourne and G. W. Gabb, *Coll.*, 1916, 128-134, 136-146. This Jour. **11**, 286 (1916).
30. Depilation of Hides and Skins. J. E. Pickles, *Coll.*, 1916, 153.
31. Note on the Action of Lime in the Unhairing Process. J. T. Wood and D. J. Law, *Coll.* (Lond.), 1916, 216. This Jour. **11**, 381 (1916).
32. Biological and Chemical Considerations of Hide and Pelt. I. The Relation of Elastins to the Tanning Process. W. Moeller, *Coll.*, 1918, 105-117 and 125-137, *J. S. L. T. C.*, 1918, 246.
33. Note on the Analysis of Lime-Liquors. F. C. Thompson and W. R. Atkin. *J. S. L. T. C.*, 1920, 15.
34. The Leather Chemist's Pocket Book. H. R. Procter.

Since the object in devising a satisfactory scheme for the analysis of lime-liquors is to give a quantitative representation of their properties so that an efficient control of their action can be effected in the tannery, it seems necessary first of all to consider these in some detail. In the process of liming the following effects are generally desired:—

I. Depilation.—This is produced by the softening and solubility of the epidermis in dilute alkalies, which increases with caustic soda, lime, and ammonia in the order given, and also by bacterial action. In a fresh lime the alkali will no doubt first dissolve some

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of the epidermis and coriin (or interfibrillary substance), thus producing a nutrient medium for bacteria which will secrete enzymes by whose solvent action the hair will be still further loosened. Hence in an old tannery lime-liquor, through which several packs have passed, the unhairing will be effected mainly by bacterial action though, of course, both factors still operate on the epidemis, while in arazym, the action is entirely bacterial. Hence the importance of temperature, which up to the present has not received the attention due to it. Increase of temperature produces an increase in the softening and solubility of the epidermis, and also a greater growth of bacteria.

Advantage is taken of the solubility of the epidermis in sulphide solutions, when these are used to sharpen a lime-liquor. According to Stiasny the sharpening effect depends on the simultaneous presence of hydrosulphide and hydroxyl-ions, the best results being obtained when the relative concentration of hydroxyl-ion to hydrosulphide-ion is in the ratio of 1 to 1. While an excess of hydroxyl-ions is only of little influence, an excess of hydrosulphide-ions causes a reduction in the action.

II. Swelling.—This is no doubt a function of the hydroxyl-ion concentration of the liquor, hydrosulphide-ions exerting no swelling effect, but it may be remarked that sodium hydroxide is probably taken up not only to a greater extent but also at a more rapid rate than lime. Swelling is decreased by rise of temperature, since the cohesion or elasticity (e) of the hide also diminishes with increase in temperature.

III. Solution of the Epidermis and Interfibrillary Substance of the Pelt, and of course at the same time, of hide substance, as a consequence of bacterial action which increases with increasing temperature. Bacterial action is largely determined by the age of the lime-liquor, though the effect of this seems to be complex.

Rogers (this JOUR. **9**, 42, 1914) states that new lime has a greater solvent action on hide than old lime which he attributes to the protective colloid property of the latter. Wood (*Coll.*, 1914, 305) states that there is a definite amount of nitrogenous substance which the limes are capable of extracting from the hide or skin. This amount might be looked on as a partially hydrolyzed portion, normally occurring in fresh hide, which would be soluble in either a new or old lime, but further degrada-

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tion and consequent solution is undoubtedly effected by the bacteria in an old lime such as is used in practice.

IV. Removal of the Fat.—The action of a lime-liquor in removing the fat, which would prevent the penetration of the tannin, must be mentioned. This takes place by saponification whereby an insoluble soap is produced, which is removed in later treatment, but since there is always excess of lime this property does not need to be considered in connection with analysis.

Finally it should be noticed that temperature has an influence on every effect of the lime-liquor, and by utilizing the use of an older lime or sharpening with sodium sulphide could be avoided, though with greater loss of hide substance. In spite of this, the usual chemical analysis does not take any account of it. Nevertheless the following scheme of analysis does afford an extremely useful control of the lime liquors in the tannery, where it is a question of relative values since the conditions are fixed. The problem is, of course, largely bacteriological and any chemical analysis must to a large extent measure the effects of bacterial action and therefore be indirect. The difficulty lies in the determination of the third effect, for there is at present no method of differentiating between the disintegration products of epidermal and interfibrillary matter, and those of hide substance. The following determinations furnish as complete a representation of the composition and consequent properties of a lime-liquor as our present knowledge will allow:

(i.) Depilation	Sulphides.
(ii.) Swelling	(*a*) Alkalinity.
	(*b*) Soda.
	(*c*) Salt.
(iii.) Solvent Action on Epidermis, Interfibrillary Substance and true Hide Substance.	(*a*) Acid products from epidermal matter and dissolved hide substance.
	(*b*) Amino acids present.
	(*c*) Free ammonia.
	(*d*) Total nitrogen.
	(e) Bacteriological examination.

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The lime-liquor must be freshly plunged and a sample taken by filling a stoppered half-winchester. This is allowed to stand overnight to settle and the clear supernatant solution pipetted off or in the case of a used liquor, filtered through a covered filter-paper (J. Green, 605, folded filter-paper) or centrifuged. Emphasis must be laid on the necessity of filtering to a standard degree of clearness, for as shown by Wood, the greatest care is necessary, since suspended calcium hydrate and carbonate pass through many filter-papers (Wood and Law*, *Coll.*, 1912, 121). It seems desirable that some standard method of filtering should be prescribed and adopted by members of the S. L. T. C. Centrifuging would seem to be more satisfactory for Wood and Law (*Coll.*, 1912, 122*) state that the production of an optically clear solution, involves the removal not only of particles of solid matter, but also colloidal skin substance.

I. Sulphides.—The unhairing property of a lime-liquor cannot be accurately measured since in practice the age and consequent bacterial activity have a considerable effect, but a determination of the sulphide present furnishes valuable information. The following are the principal references to the original work carried out in this connection:

The Estimation of Sulphides in Lime-Liquors. J. R. Blockey and P. V. Mehd, *Coll.*, 1912, 300. This Jour. **7**, 358 (1912).

The Determination of Alkaline Sulphides. Douglas McCandlish and John Arthur Wilson. This Jour. **8**, 28 (1913).

Criticism of above Paper. J. R. Blockey, *Coll.*, 1913, 138.

The Estimation of Sulphides in Lime Liquors. J. R. Blockey and P. V. Mehd., *Coll.*, 1914, 73. This Jour. **9**, 176 (1914).

The Analysis of Tannery Lime Liquors. H. G. Bennett, *Coll.* (London), 1915, 313. This Jour. **11**, 98 (1916).

The Determination of Alkaline Sulphides, II. D. McCandlish and J. A. Wilson. This Jour. **9** (1914), 203 and *Coll.* (London), 1916, 191.

The Estimation of Sulphide in Lime Liquors. H. G. Bennett, *Coll.* (London), 1916, 219. This Jour. **11**, 585 (1916).

The Determination of Alkaline Sulphides, III. D. McCandlish and J. A. Wilson. This Jour. **11**, 598 (1916).

The Estimation of Sulphide in Lime-Liquors, Part II. H. G. Bennett, *J. S. L. T. C.*, July, 1917, 3. This Jour. **12**, 626 (1917).

The Estimation of Sulphide in Lime-Liquors—A Reply. D. McCandlish and J. A. Wilson. This Jour. **12**, 633 (1917).

* This J. **7**, 346 (1912).

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Sodium Sulphide in Lime Liquors. H. Hayes, *J. S. L. T. C.*, 1918, 258. Abst. this JOUR. **14**, 27 (1919).

The Estimation of Alkaline Sulphide in Dilute Solution. H. G. Bennett and W. G. Bennett, *J. S. L. T. C.*, 1919, 190.

The best method for our purpose consists in titrating 25 cc. of the lime liquor with N/10 ammoniacal zinc sulphate solution using a 0.2 per cent. solution of sodium nitroprusside as external indicator. The method yields accurate results if the quantity of ammonia present in the standard solution is adjusted to within certain limits as shown by McCandlish and Wilson. This is achieved if the solution be prepared by dissolving 14.35 gm. of pure crystallized zinc sulphate ($Zn\ SO_4\ 7\ H_2O$) and 50 gm. ammonium chloride in 500 cc. distilled water in a liter flask, and then adding 25 cc. conc. ammonia (S. G. .880) and then making up to the mark with distilled water. The end point is shown by the non-appearance of the well known violet color and is quite definite to within one or two drops of the standard solution, each cc. of which corresponds to 0.0039 gm. Na_2S or to ½ cc. N/10 NaSH or NaOH derived from this sulphide by hydrolysis.

The above method yields results quite accurate enough for the concentrations of sulphide usually found in lime-liquors, but for the analysis of sodium sulphide itself it is better to distil with excess of magnesium sulphate into N/10 iodine, or better still into N/1 caustic soda. A definite excess of standard sodium arsenite solution is then added, the solution acidified, and the excess of arsenious acid is then determined in a measured quantity of this solution (rendered alkaline with sodium bicarbonate) with N/10 iodine solution as described by Bennett (*Coll.* (London), 1915, 315, This JOUR. **11**, 113 (1916)).

II.(*a*). *Alkalinity.*—The difficulties which have arisen in this connection are largely due to the fact that the exact significance of this factor has been overlooked in the attempt to obtain concordant results. The swelling action of a lime-liquor, of which this is a measure, is no doubt due to the hydroxyl-ion concentration and is governed by the same laws which hold in acid swelling (The Swelling of Gelatinous Tissues. H. R. Procter and D. Burton, *Coll.*, 1916, 114). Alkaline swelling has not been thoroughly investigated from this point of view though the author hopes to take this subject up again now the war is over. The swelling of

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fibrin in alkalies has, however, been studied. (R. C. Tolman and R. S. Bracewell, *J. A. C. S.*, 41, 1,503, Oct., 1919 and *J. S. L. T. C.*, 1919, 231-2. The Molecular Mechanism of Colloidal Behavior).

The obvious method of determining the alkalinity is to titrate the lime-liquor with N/10 hydrochloric acid but the difficulty lies in the choice of a suitable indicator.

Methyl orange would give not only the total alkalinity, but that due to hydrosulphide-ions, which according to Stiasny do not swell the hide. The end point also is not sharp since it is affected to some extent even by the peptone matters derived from the action of lime on hide substance. Phenolphthalein would give roughly the caustic alkalinity (due to lime and caustic soda) but the results are inaccurate due to the ammonia present. Alizarin paste which can be used for determining ammonia, is sensitive to weak acids and therefore cannot be used on account of the sulphuretted hydrogen present, and of course, the solution cannot be boiled on account of the ammonia. Methyl red is also quite unsuitable on account of its sensitiveness to sulphuretted hydrogen. Hence an indicator is required which will estimate lime, caustic soda, ammonia and at the same time be insensitive to weak acids like sulphuretted hydrogen. In the absence of an indicator which will do this under the conditions present in a lime-liquor, the only satisfactory and logical method seems to be to determine firstly the total alkalinity. This is done by boiling the lime-liquor with excess of N/10 sulphuric acid till all the sulphuretted hydrogen is expelled, and then titrating the excess of acid with N/10 caustic soda and methyl red or alizarin. The details of the method as described by Bennett in his excellent paper (*Coll.*, (London), 1915, 260, This Jour. **11**, 101 (1916), are as follows:

"Twenty cc. N/10 H_2SO_4 are pipetted into a 6 inch porcelain basin and 10 cc. filtered lime-liquor are then pipetted into the acid. The mixture is diluted to about 60 cc. with distilled water and then boiled vigorously for 2-3 minutes, stirring constantly with a glass rod. The burner is then removed, and after adding any distilled water that may be necessary to make the volume about 30 cc. the liquor is titrated with N/10 caustic soda. Either methyl red or alizarin may be used as indicator, the same results

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being obtained. The author has not found duplicate titrations to differ by more than 0.1 cc."

This determination, however, includes the alkalinity derived from:

(*a*) calcium hydroxide or lime,
(*b*) sodium hydroxide,
(*c*) sodium hydrosulphide,
(*d*) ammonia,
(*e*) the lime in combination with the weakly acid decomposition products of the hide and epidermis.

In dealing with lime-liquors we are on the rising portion of the swelling curve and since at these dilutions calcium hydroxide and sodium hydroxide will be completely dissociated, we arrive at the following conclusions in analyzing this result. Firstly—the swelling increases with the concentration of calcium hydroxide and sodium hydroxide but not to the same extent with the ammonia. Secondly—sodium hydrosulphide has no swelling action. Thirdly—the lime salts of the weakly acid decomposition products will depress the ionization and also the solubility of the lime and consequently the swelling. This fact and the protective colloid effect explain, at any rate to some extent, the poor swelling action of old limes. The sodium hydrosulphide concentration can easily be calculated from the amount of sulphide present and deducted from the total alkalinity, and hence a figure obtained which is composed of factors which all influence the swelling and hence determine its value. Since the ammonia can easily be estimated, the lime in combination with the acid decomposition products could be determined if the caustic alkalinity—that is the alkalinity due to caustic lime and caustic soda—could be found. The most pressing need at present is for a rapid, theoretically sound method of determining this. Most of the methods suggested include the lime of the lime salts and the best method available seems to be the development of Stiasny's application of Schiff's reaction (involving the use of formaldehyde), described by Bennett (*Coll.*, (London), 1915, 321, This Jour. **11**, 121). There is, however, a serious inaccuracy in this method, but a modification has been worked out by W. R. Atkin and W. E. Palmer, which will be published very shortly.

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II. (*b*). *Soda.*—A determination of the soda is very rarely wanted, for it is included in the alkalinity. When required, it is estimated by precipitating the lime and some organic matter from a definite volume of lime-liquor, with ammonia and ammonium oxalate. The filtrate is then evaporated and ignited and the residue extracted with boric acid. This is then titrated with N/10 acid and methyl orange, and the acid consumed gives the total soda as derived from both the hydroxide and sulphide. Bennett (*Coll.* (London), 1915, 317, This JOUR. **11**, 116) gives the details as follows:

"Into a 200 cc. graduated flask are pipetted 100 cc. filtered lime liquor and 10 cc. 10 per cent. ammonia are added. The flask and contents are heated to boiling point on the water bath. In a beaker or beaker-flask 20 cc. saturated (4 per cent.) ammonium oxalate solution and 10 cc. 10 per cent. ammonia are also heated to boiling point, and then added to the hot lime-liquor. The contents of the 200 cc. flask are digested on the steam bath for 10-15 minutes, cooled to 15°C., made up to mark and mixed well. The liquor is filtered through a suitable dry filter, and 50 cc. of the clear filtrate (corresponding to 25 cc. original lime liquor) are evaporated to dryness in a platinum basin. The residue is ignited strongly, dissolved with the help of 25 cc. of warm 3 per cent. boric acid solution, washed into a 300 cc. conical flask and titrated with N/10 acid and methyl orange."

II. (*c*). *Salt* has been included because of its reputed depressant action on swelling and also its solvent action on hide substance, since it is very liable to be carried into the lime-liquor in dealing with salted raw material. Its determination, however, is of little value unless it is proved to have an appreciable influence on the liming process. Griffith has stated that salt has no influence on alkaline swelling and its solvent power for hide substance seems to be very small, and where a loss of hide substance does occur, it is due to the insufficient quantity used to prevent bacterial action. This is the finding in the Committee Report of 1917 on The Solubility of Hide in Salt Solutions, by L. Balderston (This JOUR., 193-198 and 265, 1917).

The most reliable method seems to be that in which sulphides and organic matter are precipitated by zinc nitrate, the filtrate

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oxidized with nitric acid, and an excess of standard silver nitrate added, which is titrated back with N/10 potassium thiocyanate after filtering. The exact procedure is as follows (Bennett, *Coll.* (London), 1915, 334, This JOUR., **11**, 129):

"Twenty-five cc. settled lime-liquor are pipetted into a flask which already contains 25 cc. 10 per cent. zinc nitrate solution. After mixing well the contents are filtered. Into a 200 cc. graduated flask 10 cc. of the filtrate are pipetted, about 20 cc. 10 per cent. nitric acid, and about 50 cc. distilled water are then added. The mixture is heated to boiling point on a water bath and 25 cc. N/10 silver nitrate solution are pipetted into the hot liquid. On mixing with a rotatory motion the precipitate of silver chloride soon collects into large particles, the presence of the excess nitric acid assisting in this direction. The contents of the flask are cooled to 15°C., and made up to mark with distilled water. After mixing, the liquid is filtered and 100 cc. filtrate are titrated with N/10 potassium thiocyanate solution."

III. (*a*). *Acid Products.*—A control method of determining the Acid Products derived from dissolved hide substance and epidermal matter (which are rendered soluble by the action of the lime, ammonia, and ferments, and gradually broken down by hydrolysis in stages to albumoses, peptones, amino-acids, and by bacterial action to amines, etc.) lies in the difference of the titration figures with phenolphthalein and methyl orange. This difference equals the acid used in neutralizing the weak alkalies and the lime of the calcium salts of mucins, peptones, amino-acids, etc., the acids liberated being too weak to affect methyl orange, but strong enough to decolorize phenolphthalein; 25 cc. of filtered lime-liquor is titrated with N/5 hydrochloric acid and phenolphthalein; then methyl orange is added and the titration continued until the red color appears (Bennett, Commercial Control of Tannery Lime Liquors, *Coll.*, 1909, 194, This JOUR. **4**, 143 (1909)). The end point is indefinite with old limes and the method is not applicable when sulphides are present:

Example:

Titration with phenolphthalein	Titration with methyl orange	Difference
3.45	5.1	1.65
3.4	5.0	1.6

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Bennett has stated that these differences are proportional to the amount of dissolved hide substance in any given liquor, which could only be the case if hide substance and epidermal matter were attacked in constant relative proportions throughout liming, which is manifestly improbable. Although possibly of some value in works control the method has been shown by Wood and Stiasny to be inaccurate, and is quite unnecessary with the scheme here suggested.

III. (*b*). *Amino-Acid* present. Stiasny (*Coll.*, 1910, 181, Abst., this JOUR., **5**, 345 (1910)) differentiates the various forms of decomposed hide substance by an application of Schiff's reaction, in which amino-acids, which are neutral to phenolphthalein are increased in acid character by condensation with formaldehyde:

$$R\begin{cases}NH_2\\COO\end{cases} + H.CHO \rightarrow R\begin{cases}N=CH_2\\COOH\end{cases} + H_2O.$$

Twenty-five cc. of filtered lime-liquor is neutralized with acid to phenolphthalein, and a faint pink color produced by a drop or two of N/5 caustic soda. Ten cc. of neutral 40 per cent. formaldehyde is added and the acidity thus produced titrated with N/5 alkali.

The lime-liquor previously referred to, and which contained 0.75 grm. ammonia per liter gave the following results:

cc. N/5 NaOH for acidity developed	cc. N/5 NaOH to neut. 10 cc. formaldehyde	
1.6	0.9	
1.6	0.95	Mean difference = 0.7
1.5	0.9	

The method is useful in works control for effecting comparisons of the state of a lime-liquor as it gets older. If, however, sulphides are present, they react with formaldehyde, increasing the alkalinity:

$$H.CHO + NaSH + H_2O \rightarrow H.CH\begin{cases}OH\\SH\end{cases} + NaOH.$$

This can be overcome since:

$$NaSH + I_2 \rightarrow NaI + HI + S.$$

Twenty-five cc. of the filtered lime-liquor is rendered slightly acid to phenolphthalein with acetic acid. N/10 iodine (approx.)

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is run into the liquor until in slight excess as seen by the yellowish color. N/5 NaOH is now added until a distinct pink color is produced, and then 10 cc. formaldehyde. The titration is then carried out as above.

Stiasny has shown that it is possible from this and the total nitrogen figure to calculate the degree of hydrolysis of the dissolved nitrogenous matters derived from the hide, epidermis and hair. If the mgm. nitrogen which correspond to an acidity equivalent to 1 cc. N/5 alkali be calculated (a), it will be found to lie between 178 (the figure for gelatin representing no hydrolysis) and 4 (the figure for the products of complete hydrolysis of gelatin), and hence the percentage hydrolysis of the dissolved nitrogenous matter is:

$$\frac{100\,(178 - a)}{(178 - 4)}.$$

It must be noted that this shows the degree to which the disintegration of protein derivatives in the lime-liquor has proceeded, but unfortunately it does not distinguish between amino-acids derived from epidermal matter and those from true hide substance.

III.(*c*). *Free Ammonia.*—A lime-liquor contains nitrogenous matter in all stages of hydrolytic decomposition including some just at the point of breaking down into ammonia. Hence in a simple distillation it is impossible to tell when the whole of the free ammonia has come over, since both free ammonia and hydrolytically produced ammonia are being continuously liberated. For example cystine, from the proteins of the hair and epidermis, is quite easily decomposed by such a weak alkali as magnesium hydroxide at 100°C. The following method, in which this further liberation of ammonia is reduced to a minimum, is recommended:—50 cc. of the lime-liquor are pipetted into a distilling-flask and made acid to methyl orange with hydrochloric acid. Excess of freshly calcined magnesium oxide is then added, which renders the liquor only very slightly alkaline and therefore precipitates much of the nitrogenous matter and prevents frothing. It is better simply to add 10 cc. of 10 per cent. crystallized magnesium sulphate to the liquor which achieves the same result. The flask is connected with a Liebig condenser and the ammonia

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distilled into 25 cc. N/10 hydrochloric acid for 35 minutes (15 minutes, as recommended by Bennett, is too short), and the excess titrated back with N/10 caustic soda and methyl orange (on account of sulphuretted hydrogen):

$$MgSO_4 + 2NaSH + H_2O = Na_2SO_4 + Mg(OH)_2 + H_2S.$$

The method, advocated by F. C. Thompson and K. Suzuki (J. S. L. T. C., 1917, 140), in which the distillation is carried out in vacuo at 25°C.—40°C. for 30 minutes (using turpentine to prevent frothing) yields more accurate results and should therefore be adopted since under these conditions cystine is unaffected.

The use of 50 cc. of 3 per cent. boric acid, instead of a known quantity of standard acid, seems worthy of more attention than it has received, since only one standard solution would be required.

With regard to the unhairing action of an old lime, Stiasny states that the ammonia, despite the fact that it has a greater depilating effect than either lime or caustic soda, does not need to be seriously considered since the effect is mainly bacterial. Nevertheless the ammonia figure is very useful as a criterion of the age of the liquor. Further experiment seems to be desirable to ascertain what solvent action it has on hide substance and also what influence it has on the swelling in concentrations such as those in which it occurs in lime-liquors. The formation of lime-ammonia complexes of the type $Ca(NH_3)_8X$ might influence these actions.

III. (d). Total Nitrogen or Dissolved Hide Substance.—In liming, the hair and epidermis, the interfibrillary or cementing substance and, to an extent which it is desirable to limit as much as possible, the hide substance, are hydrolyzed forming with the lime calcium salts of albumins, peptones, amino-acids, and also ammonia. All these products contain nitrogen and hence its determination is of value to the tanner as a criterion of "mellowness" and bacterial activity though no method has up to the present been worked out which differentiates between the nitrogen obtained from the hide substance and the hair and epidermis. Total nitrogen is determined as follows:—25-50 cc. of the filtered lime-liquor is placed in the Kjeldahling flask, 15 cc. conc. sulphuric acid added, and gentle heat applied for about half-an-hour. The mixture is allowed to cool slightly, 5 gm. of potassium sul-

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phate added, and is then boiled vigorously till quite colorless. The heating is continued for two hours after this point. After cooling and diluting with 200 cc. of water 60 cc. of 40 per cent. caustic soda is poured slowly down the side of the flask which is immediately connected with a condenser and 50 cc. N/10 hydrochloric acid as receiving liquid. Porous pot may be used to prevent bumping or the device described by Golding (J. S. L. T. C., 1919, 72), which consists of a piece of glass tubing, of any convenient length and 4 mm. bore, sealed at one end and the walls fused together about one inch from the other end. The liquid is distilled for 35 minutes. The excess of hydrochloric acid is titrated back with N/10 caustic soda using carminic acid as indicator. Each cc. N/10 HCl neutralized by the ammonia corresponds to 1.4 mg. N or 7.86 mg. hide substance.

III. (*c*). *Bacteriological Examination.*—Plate culture in Petri dishes with a slightly alkaline peptone gelatine from which cultures of the different organisms could be prepared would seem to be of use in dealing with a lime-liquor of uncertain age. This would give an idea of the number of colonies capable of liquefying gelatine, which would be of value since it is probably only these which would cause injury to hides or skins.

Summary.

In conclusion the following scheme is suggested as a provisional method of presenting the results of the analysis of a lime-liquor, the actual determinations being carried out by the methods described in this paper, except in the case of caustic alkalinity for which see a paper to be published shortly by W. R. Atkin and W. E. Palmer.

Analysis of Lime-Liquor.

		cc. N/10 HCl per 100 cc. lime-liquor
I.	*Sulphides* { *s* cc. N/10 $ZnSO_4$ solution per 100 cc. lime-liquor, lbs. per 100 gallons lime-liquor.	
II.	*Total alkalinity*	a
III.	*Caustic alkalinity* (NaOH and $Ca(OH)_2$)	c
IV.	*Sodium hydrosulphide* (NaSH)	½ s
V.	*Ammonia*	m
VI.	*Lime in combination with weak acids* ..	a—(c+½s+m)
VII.	*Kjeldahl figure* .. K ≡ 1.4 K mg. N ≡ 7.86 K mg. hide-substance.	

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VIII. *Stiasny figure* { x cc. N/10 NaOH per 50 cc. lime-liquor.

$$a = \frac{2.8\,K}{x}.$$

$$\text{Degree of hydrolysis} = \frac{100\,(178 - a)}{(178 - 4)}.$$

IF REQUIRED:

IX. *Soda* $\equiv$ d cc. N/10 HCl per 100 cc. lime-liquor.

X. *Salt*, gm. per 100 cc. lime-liquor.

XI. *Bacteria* are (are not) present capable of liquifying gelatine.

It is necessary to adopt a definite mode of filtration which will give a constant degree of clearness and the author hopes to investigate the influence of the various factors on swelling and depilation as follows:

(*a*) The effects produced on the unhairing and swelling by calcium and sodium hydroxides in the same relative proportions and over the same range of concentrations and temperatures found in lime-liquors in the tannery.

(*b*) The effect produced on both the unhairing and swelling by adding ammonia to the above solutions over the same range of concentrations as found in practice.

(*c*) The effect produced by adding calcium salts to the solutions in (*b*).

(*d*) These experiments would be carried out in duplicate, care being taken to completely exclude bacteria in one set in order to determine the relative effect of bacteria and alkalies on depilation and swelling in lime-liquors.

HYDRATION AS AN EXPLANATION OF THE NEUTRAL SALT EFFECT.*

By John Arthur Wilson.

A mass of experimental data now available seems to indicate that the addition of sodium chloride to an acid solution results in an increase in hydrogen-ion concentration, whereas adding it to an alkaline solution causes an increase in concentration of the

* Reprinted from *J. A. C. S.*, **42**, 715 (1920).

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hydroxide ion.[1] This is of very great importance in the manufacture of leather, although probably not more so than in other fields of chemistry.

An interesting practical example of this property of salt is furnished by a series of experiments in chrome tanning recently carried out by the writer. A commercial chrome liquor (a solution of basic chromic sulphate and sodium sulphate) diluted to contain 17 g. of chromic oxide per liter was found to be capable of completely tanning certain pickled[2] calfskins in less than 2 days without any addition of alkali. A piece of chrome leather is considered fully tanned when it will remain apparently unaltered in boiling water for 5 minutes. In tanning successive lots of skins with this liquor, no difficulty was experienced in maintaining conditions so nearly constant that no difference could be detected either in the rate of tanning or in the properties of the resulting leather. The experiment was then repeated with all conditions exactly the same as before except for the addition of one lb. of sodium chloride per gallon (120 g. per liter) of chrome liquor. Measurements with the hydrogen electrode showed that an increase of about 50% in hydrogen ion concentration resulted from this addition of salt. After the skins had been in the liquor for 7 days, they were still not tanned and it was necessary to add a considerable amount of alkali to bring about complete tannage. A very similar effect is produced by adding hydrochloric acid instead of salt.

The effect of sodium chloride upon alkaline solutions is shown by adding salt to a lime liquor, which consists of a solution kept saturated with calcium hydroxide by means of a large excess and containing a comparatively small amount of sodium sulphide. The function of this liquor is to destroy the Malpighian layer of the epidermis of the skins so that the hair may simply be rubbed off by working on a suitable machine. Adding salt to such a liquor was found to increase the plumpness of the skins and to cause

[1] Poma, *Z. physik. Chem.*, **88**, 671 (1914); Arrhenius, *ibid.*, **31**, 197 (1899); Harned, *J. A. C. S.*, **37**, 2460 (1915); Fales and Nelson, *ibid.*, **37**, 2769 (1915); Thomas and Baldwin, *ibid.*, **41**, 1981 (1919).

[2] The pickling process consists of subjecting unhaired skins to a bath of sulphuric acid and sodium chloride of definite strength until equilibrium is established.

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the hair to slip somewhat more easily. This same effect is produced by the addition of sodium hydroxide.

The chrome tanning experiments noted above were a continuation of a series of simpler experiments by Wilson and Kern,[1] of which the following is typical. 0.1 *N* sodium hydroxide was added to 10 cc. of a filtered chrome liquor, with suitable agitation, until the first permanent turbidity appeared, due to precipitation of basic chromic salts, the amount required being 3.7 cc. To another portion of 10 cc. was added 0.04 gram molecule of sodium chloride; in this case 6.8 cc. of the standard alkali was required to start precipitation. Repeating the experiment, using in each case 10 cc. of the chrome liquor and 0.02 gram molecule of added salt, Wilson and Kern found different salts to have very different degrees of effectiveness in preventing precipitation, the order being $KCl < NH_4Cl < NaCl < MgCl_2 < MgSO_4 < Na_2SO_4 < (NH_4)_2SO_4$. The liquor containing potassium chloride required only 4.0 cc. of 0.1 *N* sodium hydroxide to start precipitation against 11.6 cc. for ammonium sulphate.

The order of these salts led Wilson and Kern to the conclusion that the effect was probably due to hydration of the added salt. Chrome liquors are all decidedly acid in reaction, and, if the added salt becomes hydrated at the expense of the solvent, the ratio of moles of acid to moles of solvent, and consequently the activity of the acid, will be increased, the more so the greater the degree of hydration of the added salt.

This explanation was regarded as sufficient until Thomas and Baldwin[2] proved by electrometric measurements that while chlorides actually do increase the hydrogen-ion concentration, not only of chrome liquors but of pure acid solutions as well, sulphates behave very differently, generally lowering the hydrogen-ion concentration, just the reverse of what might have been expected from the results of Wilson and Kern.

One remarkable feature of the results of Thomas and Baldwin is that when the logarithm of the concentration of hydrogen ion is plotted against concentration of added salt in the case of the alkali chlorides, the curves are apparently straight lines, of the general formula

[1] This Jour., **12**, 445 (1917).

[2] *Loc. cit.*

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$$\log [H^+] = a + bm \qquad (1)$$

where b is a constant, a the hydrogen-ion concentration with no added salt, and $[H^+]$ the hydrogen-ion concentration in the presence of m moles per liter of added salt.

Since all that remained to make this equation a valuable instrument for the rapid estimation and control of the hydrogen-ion concentrations of pickle liquors was the determination of b for various strengths of acid, the writer, assisted by Mr. Rudolph Olson, repeated the work of Thomas and Baldwin for other strengths of sulphuric acid and sodium chloride, using the same method and type of apparatus which they describe, excepting for the substitution of a Leeds & Northrup potentiometer for the Wolff bridge. The temperature, which was not controlled, varied between 18 and 22°. Our results for N, 0.1 N, and 0.025 N sulfuric acid, together with those of Thomas and Baldwin for 0.0005 N acid, are shown in Table I and Fig. 1.

TABLE I.—EFFECT OF NaCl UPON HYDROGEN-ION CONCENTRATION OF SOLUTIONS OF SULPHURIC ACID.

Moles NaCl per liter	Log [H+] of N—H_2SO_4	Log [H+] of 0.1 N—H_2SO_4	Log [H+] of 0.025 N—H_2SO_4	Log [H+] of 0.0005 N—H_2SO_4
0.000	—0.36	—1.22	—1.72	—3.50
0.428	.....	—1.13	—1.62	.....
0.856	.....	—1.04	—1.56	.....
1.000	—0.15	.....	.....	—3.29
1.284	.....	—0.96	—1.45	.....
1.712	.....	—0.87	—1.37	.....
2.000	+0.03	.....	.....	—3.10
2.140	.....	—0.77	—1.27	.....
3.000	+0.24	.....	.....	—2.92
3.210	.....	—0.55	—1.05	.....
4.000	+0.45	.....	.....	—2.71
Value of b	0.20	0.21	0.21	0.20

Apparently the curves are not only straight lines, but all four have the same slope, the average value for b being 0.205. The large percentage increase in hydrogen-ion concentration upon the addition of four moles per liter of sodium chloride and the fact that it is practically the same, about 560%, for widely different strengths of acid, suggest that the effect must be due to some action of the salt upon the solvent, such as hydration. It is of course apparent that any increase in concentration of acid caused by hydration of

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the salt will result in a lesser percentage ionization of the acid, but at least 2 factors, other than hydration of the salt, will tend to cause an increase in hydrogen ion concentration, and these are the hydration of the acid itself and the fact that with increasing salt concentration there will be less total water, free and combined, per liter of solution. If these opposing tendencies exactly balance each other, that is, if they operate so that the percentage increase in hydrogen-ion concentration found is equal to the percentage increase in concentration of total acid, then it is an easy

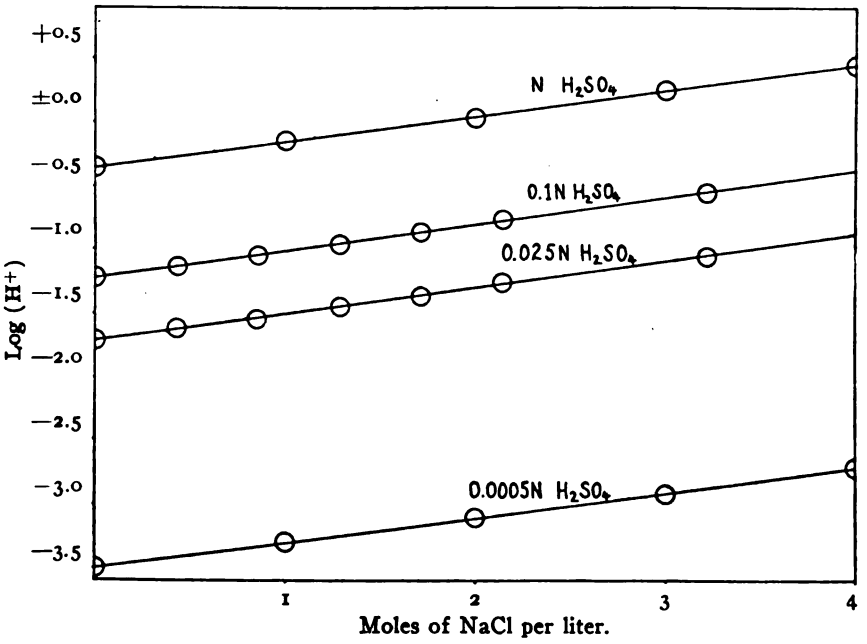

Fig. 1.

matter to calculate the degree of hydration of the salt for any concentration. The fact that we get the same slope for all four curves seems to show that here the opposing tendencies are nearly balanced. Nevertheless, this may not prove true for other cases, so the safer plan would be to select acid solution so dilute as to make these opposing tendencies of negligible magnitude. It would appear, however, in the case of sulfuric acid, that $b =$ 0.205 for sodium chloride in all concentrations of acid less than normal. Let us, therefore, calculate the degree of hydration of

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salt in a solution of acid so dilute that we may neglect the hydration of the acid and its partial volume and consider it totally ionized.

From Equation 1 $\log([H^+]/a) = bm$. But $[H^+]/a$ is the factor by which the acid concentration has been multiplied by adding m moles per liter of salt. Let w represent the total number of moles of water, free or combined with salt, in one liter of solution containing m moles of salt. The moles of free water then equal $wa/[H^+]$ and the moles of water combined with one mole of salt equal $(w/m) \times (1-a/[H^+])$. Calling this latter value h, we have

$$h = w\,(1 - 10^{-bm})/m. \qquad (2)$$

Substituting 0.205 for b in Equation 2, we have calculated the degree of hydration of sodium chloride for several concentrations. (See Table II.)

TABLE II.—Calculated Values for Degree of Hydration of NaCl at Different Concentrations.

Moles NaCl per liter (m)	Total moles water per liter (w)	Molecules water combined with one molecule of NaCl (h)
4.0	51.1	10.9
3.0	52.3	13.2
2.0	53.5	16.3
1.0	54.6	20.5
0.1	55.4	25.5
0.01	55.5	26.1
0.001	55.5	26.2
0.000	55.5	26.2

The striking agreement between our value 26.2 for infinite dilution and Smith's[1] calculated value of 26.5 by quite another method confirms the idea that hydration of the salt is responsible for the increase in hydrogen-ion concentration noted.

When it is required to calculate the degree of hydration only for infinite dilution, Equation 2 may be greatly simplified, since

$$\lim_{m=0} h = w(10^{bm} - 1)/m = 2.30wb = 128b. \qquad (3)$$

Conversely, given the degree of hydration at infinite dilution, one may simply divide by 128 to get b and substitute in Equation 2 to calculate hydration values for any finite concentrations, provided

[1] *J. A. C. S.* **37**, 722 (1915).

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of course the degree of hydration follows the rule expressed by Equation 2.

For the sake of comparison we made a set of determinations with N sulphuric acid and potassium chloride, the results of which are given in Table III. Since $b = 0.14$, the degree of hydration at infinite dilution would be 128 times as great, or 18, which is not far from Smith's value of 19.2.

TABLE III.—EFFECT OF KCl UPON HYDROGEN-ION CONCENTRATION OF N SULPHURIC ACID.

Moles KCl per liter	Log [H+]
0.0	—0.36
1.0	—0.21
2.0	—0.09
3.0	+0.05
Value of b	0.14

Thomas and Baldwin's results with hydrochloric acid show greater slopes for the alkali chlorides in 0.004 N than in 0.1 N acid. For each salt the value of b is less in the stronger solution by about 15% of its value in the weaker one. Since complications introduced by the acid would naturally be less noticeable in more dilute solutions, the values of b in the weaker acid may be taken as more nearly representing the true index of hydration of the salts. Values for $128b$ in 0.004 N hydrochloric acid follow: potassium chloride, 15; ammonium chloride, 15; sodium chloride, 26; lithium chloride, 35; and barium chloride, 50. Smith's corresponding values are potassium chloride, 19.2; ammonium chloride, 20.3; sodium chloride, 26.5; and lithium chloride, 33.6. Considering the limits of accuracy of the method as employed, the fact that temperature was not controlled, and that hydration of the acid and the repression of its ionization were ignored, the similarity between these two sets of results seems more than a coincidence. In fact, the writer believes it strongly confirms, for chlorides, the earlier view that the neutral salt effect is due to hydration and also the suggestion[1] that the Hofmeister series of the ions owes its nearly fixed order to the fact that the degree of hydration of the ions runs in the same order.

The peculiar behavior of the sulphates of sodium and ammonium in lowering the hydrogen-ion concentration of acid solutions,

[1] This JOUR. 13, 179 (1918).

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when one might have expected them to raise it very materially, may after all be found to be due to the same forces as bring about hydration. Their action can hardly be simply that of repressing the ionization of the acid because of their effect upon chrome liquors, whose resistance to precipitation by alkalies they increase very much more than chlorides do, and this in view of the fact that in some cases they lower the hydrogen-ion concentration to a point at which precipitation of basic chromic salts might be expected without any addition of alkali. The tendency of sulphates to form addition compounds may eventually afford an explanation.

The nearly quantitative agreement between hydration values of the alkali chlorides at infinite dilution given by Smith and those calculated in this paper from hydrogen-ion measurements seems to warrant a much more extensive pursuit of the subject and especially of the use of the electrometric method for studying hydration and its effect upon concentrated solutions.

ABSTRACTS.

Contrasting Effects of Chlorides and Sulphates on the Hydrogen Ion Concentration of Acid Solutions. By A. W. THOMAS and M. E. BALDWIN, *J. A. C. S.* **41**, 1981 (1919). The addition of sodium chloride or ammonium chloride to chrome tanning liquor increases the hydrogen ion concentration, whilst the addition of magnesium sulphate, sodium sulphate, or ammonium sulphate reduces it. Solutions of chromium sulphate, sulphuric acid (0.0005*N* and 0.1*N*), and hydrochloric acid (0.004*N* and 0.1*N*) behave similarly with both chlorides and sulphates. The power of increasing the hydrogen ion concentration follows the order:

$$MgCl_2 > BaCl_2 > LiCl > NaCl > NH_4Cl = KCl.$$

Boric Acid Modification of the Kjeldahl Method for Crop and Soil Analysis. By F. M. SCALES and A. P. HARRISON, *J. I. E. C.* **12**, 350 (1920). Winkler's[1] modification of the Kjeldahl method in which he proposed the use of boric instead of sulphuric acid in the receiving flask is found to be as accurate as when the latter reagent is employed. Ninety-five mg. of nitrogen as ammonia can be recovered in the distillate when 50 cc. of 4 per cent. boric acid is used.

Bromophenol blue is a better indicator than those used by the other investigators.

The method has the following advantages:

1. It does away with the occasional errors that arise from slight mistakes in measuring the sulphuric acid into the receiving flask.

[1] *Z. angew. Chem.*, **26**, 231 (1913).

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2. As the boric acid solution need be measured only approximately, much time can be saved, and an unskilled helper can measure it into the receiving flasks.

3. By proper adjustment of the strength of the standard acid and the weights of the samples taken the percentage of nitrogen can be read directly from the burette.

4. It is necessary to prepare accurately only one standard solution, *i. e.*, the sulphuric acid for titrating.

On the Evolution and Oxidation of Chromic Hydroxide in Alkaline Solution. F. BOURION and A. SENECHAL. *Comptes Rendus*, 30th Dec., 1918, through *Le Cuir*, 1919, *VIII*, 337. The authors, in endeavoring to make a kinetic study of the oxidation of chromic salts with hydrogen peroxide in an alkaline medium, noted that solutions of chromic salts in soda changed slowly with time and that their reducing action on the hydrogen peroxide diminished with time. It was found impossible completely to oxidize all the chrome present in alkaline solution. Using four to five times the theoretical quantity of hydrogen peroxide, 90% of the chrome present was oxidized; by adding caustic soda to a solution of chrome alum containing four times the theoretical quantity of hydrogen peroxide, and immediately destroying excess by shaking up with manganese dioxide, 97% of the chrome was oxidized. Using only the theoretical quantity of hydrogen peroxide under the same conditions only 59% of the chrome was oxidized. Similar results showing decrease of oxidation with time were obtained with alkaline solutions of potash alum, ammonia alum, and chromic sulphate.

Evolution was far more rapid with increasing concentrations of chrome salts, but was largely retarded by increasing the concentration of sodium hydroxide.

The results showed that an alkaline solution of chromic hydroxide undergoes an evolution which tends to cause it to lose in course of time all chemical activity, and especially its reducing properties, all the more rapidly as the concentration of chrome is increased and that of alkali diminished.

These results may be compared with those of Recoura (*Com. Ren.* 1895, 1335) who noted that chromic oxide obtained from its alkaline solutions loses little by little the property of dissolving in hydrochloric acid, a fact which he studied from the thermochemical standpoint.

J. S. L. T. C.

Hemlock Sole Leather—An Historical American Product. From *American Leather*, published by the Tanners' Council, through *S. & L. Rep.*, Mar. 25, 1920. A study of the location of tanneries in the United States furnishes some very interesting information with regard to the characteristic products of the leather industry. If we were to represent each tannery in the country by a dot we might wonder why there should be such a dense mass of dots in western New York, western Pennsylvania,

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and Michigan. Climatic conditions in those regions are not unusually good from a tanner's standpoint, and neither are the facilities for transportation. These are not cattle range districts, nor great packing centers. We have, in fact, to look elsewhere for the reasons for locating these tanneries; and we soon find that the establishment of nearly all of them dates back a generation or so and that more recently there has been no tendency to locate large new tanneries in these localities. A still closer survey, moreover, shows that in place of a cattle range district we have a vast wooded area, extending more or less throughout the elevated region of the eastern United States, and that throughout the more northerly districts of this area we find the principal range of a single tree—the hemlock (*Tsuga Canadensis*).

This cone-bearing tree, whose bark has about 11 per cent. of tannin, was largely responsible for the location of so many tanneries in the regions just mentioned. It was a case of saving freight on bark, for about eighty-nine parts out of each hundred parts of the bark were of little value in making leather and the use of tanning extracts was not as common a generation or more ago as it is now.

The mere fact that hemlock bark has 11 per cent. of tannin does not tell the whole story, nor yet what may have seemed at one time the impossibility of using up the visible supply of bark. Back of this is the underlying fact about which we really know so little—the fact that no two tannins from different sources are alike—tannin from hemlock bark being one thing, that from mangrove bark quite another, and that from sumac leaves yet another. Even then hemlock bark was known to have tanning properties peculiarly its own, and the trade journals of those days spoke of "acid hemlock" as one of the largest items of production.

In addition to the cheapness of hemlock bark, due to its abundance and the choice of tannery locations, there was another thing which contributed to produce cheap hemlock sole leather, that is, the use of dry hides, largely imported. These dry hides had the usual virtues and defects of this class of raw material. Their relatively lower cost as compared with the higher priced wet-salted hides, combined with the rather rapid hemlock tannage, brought it about at one time that hemlock sole was by far the largest item of sole leather produced in this country, as opposed to the production of the "Union" and oak varieties. As a natural consequence it was possible for the tanner to sell this hemlock leather for less money than many of the other tannages and with its lower price there was created a demand for export of this cheap and serviceable leather.

In the course of years this demand gained impetus and American hemlock leather gained an excellent reputation, well earned. In its class, grades, and cuts, it was uniform, good and cheap. But as the demand for the bark for tanning grew, the number of trees available for cutting and peeling decreased. As a result the price of hemlock bark steadily mounted and the favored few who owned and still own stands of hemlock have profited greatly. To-day, as explained below, there is exceedingly little straight hemlock leather manufactured.

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Straight hemlock leather has certain earmarks which serve to identify it with reasonable certainty. It is what is commonly known as a "red" leather and it is not very difficult to identify hemlock bark and hemlock bark extract from other barks and tanning extract by the color of the leather produced. There is also an unmistakable odor to the bark and extract. The only other bark so far as the writer is aware, which approximates hemlock bark in odor is the bark of the American chestnut oak, so commonly used for tanning.

The finished hemlock sole leather is always hard, rather coarse fibered, and tended to be brittle and not very flexible. It is just these qualities which makes this leather valuable for ordinary shoes made to stand wear and to take and hold fast the hobnails which are used to increase the wear of shoes subjected to rough usage. You will see that no claim is made for great flexibility or ease on the foot for hemlock sole leather, but rather for service first, last and all the time. Naturally, this leather does not lend itself extraordinarily well to Goodyear welting, but rather to thorough stitching and nailing.

This, no doubt, restricts to some extent the field of usefulness of hemlock sole. Still, for special work it may be softened by the use of glucose and Epsom salts to increase ease of cutting and handling in the shoe factory, particularly when more pliable soles are desired. Cautious oiling likewise helps to soften the grain of the leather.

Hemlock bark is an astringent tan; that is, it tends to tan rapidly. So, when using the bark or extract, it is usually necessary to plump heavily and to enter rather weak tan liquors for fear of "case hardening." As a consequence, after deliming, the hides are usually struck by a weak solution of the bark or extract until the surface is just barely tinged a reddish brown and then they are plumped with hydrochloric or sulphuric acid in the usual way, and the tanning proceeds in about the accustomed mannenr in the rockers, handlers, and layers, in varying combinations. Hemlock bark cannot be considered rich in sugar, and as a result cannot form sufficient acid when used alone. It is necessary, consequently, either to add other fermentable. tanning materials to produce acid—resulting in "union" tannages—or to have recourse to the powerful plumping acids just mentioned.

Owing to this situation—combined with the comparative shortage of the bark—nearly all of the hemlock sole leather now manufactured in the United States is, strictly speaking, a union tannage, since a considerable proportion of chestnut extract enters into the process. Even when this is done the quantity of hemlock used is apparently sufficient to tighten up the fibers of the hide to an extent sufficient to produce the ability to hold nails which, as has already been stated, is the important feature of this class of leather. This procedure has, moreover, the great advantage of making more economical use of the remaining supply of hemlock bark. Under these conditions, the hemlock sole leather industry has in sight a supply of tannning material sufficient, at any rate, for a number of years. Little or nothing has been done with a view to reforestation of the hem-

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lock producing areas and it is not certain whether this could be done economically. The special qualities of hemlock sole leather, however, are so unique that it is to be hoped that measures which may be taken will prove effective in conserving or replacing the supply.

On the Retention of Fat in Leather. By W. FAHRION, *Chemischen Rundschau* thru *Gerber* **43**, 123 (1917). The object of oiling (stuffing) vegetable leather is to bestow a higher degree of softness and flexibility than tanning alone imparts. In order to attain this object the fat should be entirely absorbed by the leather, distributed as uniformly as possible and continue to remain so. Such conditions are ideal and scarcely attainable. Frequently the higher melting point constituents of the fat remain on the outside and have to be removed before finishing can be carried on. Paessler has demonstrated that the distribution of fat in leather is not uniform. And finally, it frequently happens that the fat after being completely absorbed will partially reappear on the surface of the leather. This later condition commonly called spueing can appear in many forms. This article confines itself to that form which manifests itself by the appearance of a thin white coating of fat on both sides of the leather or only on one side, usually on the grain. It can be removed by washing with benzine or soda solution but will frequently reappear after some time. It is generally assumed that this white spue consists of saturated, free fatty acids and that spueing is preceded by a splitting of the fat.

The author examined the fat from leather that showed a distinct white spue on the flesh as well as the grain. The spue was scraped from the leather and the fat isolated from both the scrapings and an average sample of the leather. In both cases the fat was removed with ether, the ethereal solution shaken out with water to which a few drops of hydrochloric acid had been added, in order to remove tannin constituents likely to be present. Nevertheless on evaporation of the ether small amounts of brown amorphous matter separated. The residue was therefore taken up with petroleum ether, filtered and the petroleum ether removed. For the sake of simplicity the fat obtained from the leather is designated "leather fat," that from the spue, "spue fat." The "leather fat" amounted to 24.1% of the leather; the "spue fat" amounted to 2.2% of the original total fat.

The analysis of both fats was carried out uniformly in the following manner: The melting point was first determined in open capillaries with water as medium. This determination required less than 10 mg., the remainder was warmed with alcohol, phenolphthalein added, and titrated to red with N/5 caustic alkali for the acid value. Alcoholic lye was added to this and it was heated on the water bath with stirring until the alcohol had evaporated.[a] The soap was taken up with 50% alcohol and shaken out three times with petroleum ether for the determination of unsaponifiable. The alcohol was then expelled and from the aqueous soap solution, the fatty acids soluble in petroleum ether and the insoluble oxy-acids were separated by shaking with petroleum ether and hydro-

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chloric acid. The melting point and the acid value (mean molecular weight) was determined on the fatty acids. From the soap solution the fatty acids were regenerated and their iodine values (Hübl-Waller, 24 hour action) ascertained. The results obtained are as follows:

	"Leather fat"	"Spue fat"
Color	Deep yellow	Light yellow
Crystallization	Indistinct	Distinct
Melting point	39°	32°
Acid value	27.0	21.6
Unsaponifiable	3.0%	1.9%
Oxy-acids	2.2%	2.3%
Fatty-acids	90.2%	91.1%
(Hehner value)	(95.4)	(95.3)
Fatty Acids		
Color	Yellow, interspersed with white crystals	Uniformly pure white
Crystallization	Distinct	Very distinct
Melting point	39°	52°
Mean mol. wt.	277.7	279.4
Iodine value	59.8	33.8

From the above results the author concludes that the assumption previously mentioned does not always hold true. Splitting of the fat does not precede spueing as the acid value of the "spue fat" is lower than that of the "leather fat," and there is more glyceride in the "spue fat." On the other hand, doubtless a fractionation of the fat in the leather precedes spueing, in the direction that the saturated (solid) fatty acids have concentrated in the spue fat. The lighter color of the "spue fat" and greater ability to crystallize, suggests this, more so the higher melting point and lower iodine value of its fatty acids. If it is assumed that only oleic acid (iodine value 90) is present in the unsaturated fatty acids, its content in the leather "leather fat" would be two parts to one of saturated fatty acid while in the spue fat this proportion is reversed. This is difficult to reconcile with the lower melting point of the "spue fat," for in general with increase in melting point of fatty acid mixtures that of the corresponding glyceride also rises. Exceptions can be caused by different grouping of the saturated and unsaturated acids in the so-called mixed glyceride. Such glycerides can show a fairly high content of saturated, high melting fatty acids and still be fluid under 0° C. Therefore the following supposition is expressed, only, however, with reservation as it is deduced only from the foregoing experiment—spueing of a stuffed leather is to be feared, if from the glyceride mixture used for stuffing another glyceride mixture can be formed by fractionation which with a higher content of saturated acids shows a lower melting point.

The unsaponifiable was yellow, semi-solid and completely soluble in acetic anhydride. This gave the familiar reaction for wool grease—

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a deep green coloration with concentrated sulphuric acid. It may be assumed that the stuffing mixture contained about 10% of wool grease. From the content of oxy-acids in the "leather fat" and "spue fat," it can safely be assumed that the stuffing mixture also contained dégras. Both wool grease and dégras are amorphous and both are known as excellent stuffing materials for vegetable leather. The author mentions one of Knapp's principles, namely, that each true tanning material must be in amorphous form (one says to-day—colloidal) in which state it will be taken up by the fiber. To convert this principle to apply to stuffing it may be said—a fat will be so much more suitable for stuffing of leather the lower the tendency it has to crystallize. The large amount of tallow which has been used for stuffing leather stands in contradiction to this statement but it is suggested that tallow, primarily is essential as a thickening agent and that apparently, an amorphous fat of the same melting point would be preferred to it as a stuffing material for leather. It is safely assumed that in the foregoing case the stuffing material contained tallow and that the white spue originated in it. G. W. S.

PATENTS.

Process of Treating Leather. U. S. Patent 1,326,261. ALFRED J. HAWKINS, Montreal, Quebec, Canada. A process of treating leather which consists in covering the leather with a thin coating of oil heated to a temperature of approximately 150° F., then allowing the oil to remain in contact with the leather for approximately 12 hours and until the temperature of the leather has cooled to approximately 80° F., then applying a second coating of oil heated to approximately 150° F. and again allowing the leather and oil to remain in contact and cool to a temperature of approximately 80° F. for another 12 hour period, and repeating the alternative heating and cooling process until a series of coatings have been thus applied.

Leather-Splitting Machine. U. S. Patent 1,326,317. KARL ZIMMERMANN, St. Gregor, Saskatchewan, Canada. Filed Jan. 17, 1919.

Composition of Matter for Use as a Leather Substitute. U. S. Patent 1,326,681. JUSTUS W. MATTHAEI, Ingram, Pa. A vulcanized leather substitute, formed from a composition of matter composed of an excess by weight of rubber, and an excess by bulk of cork particles, in combination with a fibrous material, reclaimed rubber, sulphur and glue.

Process of the Production of Tanning Extract From Waste Sulphite Lye. U. S. Patent 1,327,105. HANS BRUN LANDMARK, Drammen, Norway. A process for the production of tanning extract from waste sulphite lye, characterized by evaporating waste sulphite lye to a concentration of about 16° to 18° Baumé; adding to the concentrated solution about 18 grams of carbonate of sodium for each liter of the amount of lye before concentration; separating the liquid from the precipitate thus obtained; and

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adding to said liquid a quantity of oxalic acid sufficient to precipitate the calcium still remaining in solution; separating the liquid from the precipitate thus obtained and adding a sufficient quantity of formic acid to decompose any saccharate that may be present; and concentrating the solution thus obtained to about 27.5° Baumé.

Glue and Process for Manufacturing the Same. U. S. Patent 1,329,599. SHERBURNE B. HENNING, Rhinelander, Wis. A glue comprising blood albumin, ammonium hydroxide, lime and water.

Dressing for Leather and Painted and Varnished Surfaces. U. S. Patent 1,329,968. WILLIAM O. HARRIS, Huntsville, Ala. A dressing for leather and painted and varnished surfaces, the same consisting of raw linseed oil 66%, apple vinegar 30%, benzine 3% and amber oil 1%.

Leather Graining, Boarding, or Softening Machine. U. S. Patent 1,330,962. JOHN E. SPENCER, Salem, Mass. Filed Sept. 19, 1917.

Composition of Matter for Use as a Substitute for Leather and Similar Purposes, U. S. Patent 1,332,320. GEORGE CHRISTENSON, Jamaica, N. Y. A dense, non-elastic composition of matter comprising rubber, finely ground sponge and a considerable proportion of an inert filler intimately mixed together.

Barking-Machine. U. S. Patent 1,333,734. IVAN ROCIC, Chicago, Ill. A barking machine comprising a rotatable drum having walls thereof formed of longitudinal angle irons having one of their legs arranged circumferentially and the other legs projecting inwardly, and said inwardly projecting legs being arranged in alternating sets of different heights.

Manufacture of Leather. U. S. Patent 1,334,216. WILLIAM C. BLATZ, Wilmington, Del. As a new article of manufacture, glazed white washable leather made from alum-chrome-treated skins or hides and having its surface, body and fibers impregnated with a barium salt in an insoluble state.

Utilizing Scrap Leather. British Patent 134,592. S. C. LANSDOWN, Melbourne, and P. MAGNUS, North Fitzroy, near Melbourne, both in Victoria, Australia. Scrap leather is reduced to powder, cleansed with oxalic acid, and then mixed with an adhesive consisting of liquid glue, boiled linseed oil, carbolized oil, and oil of cloves. The mixture is dried and pressed into sheets, etc., for use as a substitute for boot and shoe leather or otherwise.

Leather. British Patent 135,496. C. R. REUBIG, Giessen, and O. M. SEEMANN, Frankfort-on-the-Main, both in Germany. *Stretching by tension.*—A stretching-frame for regulating the tension of hides and skins during tanning is formed with a single pair of clamping jaws at one end and a series of pairs of clamping jaws at the other end capable of being adjusted conjointly or independently.

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Leather Compositions. British Patent 135,921. W. DRURY, London. In a leather-rubber composition, the following proportions may be used: 16 lbs. rubber, 20 lbs. leather flour, 5 lbs. calcined magnesia, 3 lbs. sulphur, 3 lbs. brown factis; or, for a hard vulcanite material, 32 lbs. rubber, 60 lbs. leather flour, 16 lbs. sulphur, and ½ lb. magnesia. The composition is for making boot soles, etc., and for coating canvas for printers' blankets, upholstery, etc., and the invention consists in the particular process employed. Crude, waste, or reclaimed rubber is masticated between rolls, and, while the rubber is on the rolls, an intimate mixture of leather flour, filling material, and sulphur is added thereto, a small amount of factis or like fatty material being added to the rubber while being masticated, or to the flour mixture before it is combined with the rubber, and the mastication being continued to give an intimate mixture. The temperature of the rolls is then raised to effect partial vulcanization and the material is finally passed to calender rolls prior to complete vulcanization in a platen press or an open live-steam press. The final temperature of the rolls is about 240° F. The material may be passed through a refining-mill prior to calendering. The sheets as delivered from the calender rolls, say 1-16th or 1-20th inch thick, may be superposed alternately in directions at right angles to one another in order to give strength.

Tanning. British Patent 136,193. W. CLARK, London. Iron formate is used for tanning. The pickled skins, freed from hair, may be treated with a liquor in which iron formate is produced by mixing an iron compound with formic acid or with a salt of formic acid.

Synthetic Tanning-Agents. British Patent 137,323. M. MELAMID, Freiburg, Breslau, Germany. *Sulphonic acids.*—Synthetic tanning agents are prepared by condensing aromatic sulphochlorides with the alkali-soluble fractions of anthracene oil or soft pitch, and sulphonating the condensation products so obtained. According to an example, anthracene oil or a soft pitch distillate is extracted with dilute caustic soda lye, the extract is purified and condensed with toluene sulphochloride in benzine solution, the product is sulphonated with sulphuric acid monohydrate, and the sulphonic acid converted into its sodium salt.

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CONTENTS

The First Meeting of the Section of Leather Chemistry and the Fifty-Ninth Meeting of the American Chemical Society at St Louis, Missouri - 339
President's Address to the Seventeenth Annual Meeting. By R. W. Griffith - - - - - - - - 341
The Extraction of Chestnut Wood. By C. T. Gayley - - 344
On the Volumetric Determination of Chromium in Chrome Leather. By Te-Pang Hou - - - - - - - 367
Vegetable Tanning as a Colloid-Chemical Process. By John Arthur Wilson - - - - - - - - 374
Leather and Glue. By F. C. Thompson - - - - 380

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THE FIRST MEETING OF THE SECTION OF LEATHER CHEMISTRY AND THE FIFTY-NINTH MEETING OF THE AMERICAN CHEMICAL SOCIETY AT ST. LOUIS, MISSOURI.

On Wednesday morning, April 14th, the Leather Section of the American Chemical Society held its first meeting at St. Louis with Chairman Louis E. Levi and Secretary Wm. Klaber in charge. The program was as follows:

Address of welcome by the Chairman.

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An illustrated lecture by Dr. Edward E. Marbaker of Alexander Bros. on the currying of leather for belting.

A paper by J. A. Wilson and Edwin A. Gallun showing that the addition of salt to any tannery liquor has the same effect upon the process as using a stronger liquor, which they explain by hydration.

Dr. Arthur W. Thomas exhibited a new method for determining the amount of free sulphuric acid in leather.

E. J. Kern gave a new method for determining sulphate in sulphonated oils which was inspired by Dr. Thomas' work on sulphuric acid in leather.

A. W. Thomas and S. B. Foster outlined a new method for finding the acidity or basicity of chrome liquors by means of the measurement of electrical conductivity.

Dr. Levi gave a talk on chemical work in the tannery. He reviewed the difficulties experienced by the leather chemists of twenty years ago and showed how prejudices had been overcome until now the chemist is a real factor in the manufacture of leather.

Mr. Kugelmass' paper on the physico-colloidal interpretation of the tanning process was held over because the author was unable to be present.

A. W. Thomas and M. J. Kelly presented an interesting account of the progress of their work on the chemistry of chrome tanning. They pointed out that their present work is only one small unit in a very extensive work that may cover a period of several years.

The paper by J. A. Wilson and E. J. Kern on the true tanning value of vegetable tanning materials aroused much discussion. The authors claimed that the present official method of tannin analysis is wrong in principle, since the detannized liquor is kept while the tanned powder is thrown away. The authors claim the new method determines how much actual leather a pound of extract will make.

On Thursday, April 15th, a colloid symposium was held. Jerome Alexander's paper dealt with practical applications of colloid chemistry. Professor Bancroft spoke on "Gelatinous Precipitates," and Professor Fischer on the "Colloid Chemistry of Soaps." J. A. Wilson then gave a talk on "Vegetable Tanning as a Colloid-chemical Process." A. V. Bleininger treated the

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subject of Ceramics and W. D. Harkins lectured on "Surface Energy." Professor Thomas completed the program by a plea for reform in the matter of nomenclature in colloid chemistry so that the path may be made easier for students just beginning a study of colloid chemistry.

PRESIDENT'S ADDRESS TO THE SEVENTEENTH ANNUAL MEETING.

By R. W. Griffith.

Fellow Members of the American Leather Chemists Association:

It is once more my pleasure and privilege to welcome you to our annual convention, which marks the seventeenth year of our existence as an Association. Seventeen is an age usually associated with the highest enthusiasm of youth, and I am glad to say that our Association is no exception to this rule. We continue to show a steady and healthy growth and while there has developed some restlessness, and perhaps some impatience, in a desire to make more rapid strides, these indications are not unnatural in the growth and development of a sound body. While it would be deplorable if we permitted ourselves to over indulge in self satisfaction with our achievements, there is abundant evidence surrounding us that the most enduring progress is that which is gradual and sound in its foundations. The administration of your Association has not been without a certain spirit of conservatism and mature judgment will no doubt concede the wisdom of this. In the field of endeavor, which is our particular choice, successful practice has rarely conformed to hypothesis and the application of a scientific truth has so many considerations involved, the lack of appreciation of which, frequently obscures its success.

As an Association we are fortunate in having nearly all our founders and original members still actively engaged in the problems of the tanning industry and their interest and enthusiasm in the work of the Association has been continuous, and while experience may have tempered their enthusiasm, it is largely due to the work of these members who have borne the heat and burden of the day, that the present day chemist enjoys some recognition in the practical operation of the tannery.

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The purpose of this Association is sufficiently broad to afford ample opportunity to any scientific investigator to contribute to the fund of knowledge, and we are ready at all times to welcome workers from other scientific fields. It may be well to remind ourselves of the objects of our Association as set forth in the by-laws:

1st. To devise and perfect methods for the analysis of leathers and all materials used in connection with their manufacture.

2nd. To promote the advancement of chemistry especially in regard to its application to problems confronting the leather industries.

3rd. To publish the results of investigation and research dealing with the above objects.

It is clear, therefore, that the Association offers every encouragement to scientific research bearing upon the problems of the leather industry, as well as the perfecting of analytical methods. It is true that efforts to perfect analytical methods have received the greatest attention from the Association and there is no need to offer an apology for this feature of our work, but on the contrary should afford us considerable pride. Leather and the materials which enter into the production of it are the most complicated in their chemical structure in the whole list of known chemical substances and the great majority of these materials do not lend themselves to the expression of chemical equations. That such materials can be analyzed by methods which yield approximately uniform results in the hands of different analysts is, in itself, an achievement of which the members of the Association may be justly proud. The laboratories of other industries dealing with well known and definite chemical compounds are not able to parallel the uniformity obtained by the leather trade laboratories. The analytical report of the tannery laboratory is something more than an indication of the composition of a tannin liquor, it is a valuable guide in the operation of the tannery and plays an important part in securing successful results, and consequently a wide range of error in the laboratory is not permissible because of its effect upon the operation of the plant. It is not claimed that the analytical methods of this Association have reached perfection. They are constantly being investigated by committees appointed

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for that purpose by this Association, and improved upon, and vigilance in this direction should not be relinquished. Analytical methods are the fundamental basis of research and unless we have reasonable accuracy in our methods of analysis, we cannot accomplish much by research.

Research work in the leather industry has made steady progress during the past year and the outlook is promising for the future. Investigations in colloid chemistry have a particular interest for the leather chemist and we are fortunate in having on our program for this meeting some papers which treat with this phase of leather chemistry and we may look forward to valuable contributions to our knowledge of the tanning industry from this field of research.

A number of Committee reports will be submitted for your consideration at this meeting, and the thanks of the Association are due to those who have contributed of their time and labor to this important work which is essentially altruistic.

In connection with our Committee work, we have received a valuable suggestion from our European friends, the Society of Leather Trades Chemists, to the effect that joint committees consisting of members from both organizations be appointed to work on problems of mutual interest. This proposal is worthy of our heartiest support and it is hoped that the new council which will take office at the close of this Convention will take steps to put it into effect.

Referring again to the question of research work in the tanning industry, attention must be called to the work which is being carried on independently of this Association by the tanners organization, the Tanners Council. It is a matter of gratification to leather chemists that the tanners of this country appreciate the importance of chemical research to endow and support a special laboratory for the carrying on of this special work. The interest of the members of this Association is particularly invited in the work of the American Leather Research Laboratory, the Director of which is anxious to secure the individual co-operation of every member of this Association.

An historical writer once observed that democracies were conspicuous for their ingratitude to those who served them best. Our Association is constituted upon democratic principles, but

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whether we are guilty of the charge of ingratitude to those who have served us faithfully and patiently without reward and with little praise for many years, is not proven. While we may have lacked in expression, we have fully appreciated the service which our officers have so unselfishly given to our Association, and on behalf of the Association, I embrace this opportunity to voice the thanks and grateful appreciation of all the members of this Association to Mr. H. C. Reed, who has served this Association as Secretary-Treasurer continuously since its formation seventeen years ago, except for a short interval when he occupied the Presidency. I would also refer to the exceptional service which Mr. W. K. Alsop, the Editor of our JOURNAL, has rendered to the Association, and on behalf of all our members I tender him our thanks and grateful appreciation.

As the years roll on witnessing the growth of our Association, I trust that the spirit of comradeship may flourish with it and that our service to the industry may continue to prosper. Our Association was conceived in the spirit of co-operation of each individual member and responsibility for the continued success of our Association rests with each one of us, or as Kipling so aptly pointed out the road to success:

"It ain't the guns or armament,
Or the funds that they can pay,
But the close co-operation
That makes 'em win the day.
It ain't the individual,
Or the army as a whole,
But the everlasting teamwork
Of every bloomin' soul."

THE EXTRACTION OF CHESTNUT WOOD.

By C. T. Gayley.

Rec'd. March 18, 1920.

There are two general methods employed in the extraction of tannin from chestnut wood. The one is the open leach method in which a temperature of 212° F., or less, is used, the wood is subjected to from ten to twenty-six changes of water and the time that the wood remains in contact with the water varies from twelve hours to three or four days. The other method of

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extraction is carried out in autoclaves, under pressure, and at temperatures ranging from 130° F. to 270° F. The object of the work presented in this article was to learn the exact merits of each of these methods and more especially to learn the exact conditions, under which to extract chestnut wood, to obtain the best yield of tannin and the purest extract in the shortest time.

It is hoped that some old matter may be presented in a little different manner, and some new matter in such a way that it will be both interesting and instructive to those interested in the problem of extracting chestnut wood. Due to the difficulty of making a complete survey of all the literature that may possibly have been published on the subject, we beg to be excused if we at any place seem to have taken as our own, data and ideas previously published, and we ourselves do not pretend to have made an exhaustive study of the subject.

There are six prime factors to take into consideration, in the extraction of chestnut wood: (1) the solvent used, (2) the temperature of the solvent used, (3) the time of extraction, (4) the ratio of the volume of wood to the volume of solvent used in the extraction, (5) the preparation of the wood, and (6) the number of washings or changes of water to which the wood is subjected.

Nearly every extract manufacturer has a little different idea as to the relative value of the various factors. Some indeed seem almost to disregard one or the other of the prime factors, while placing special emphasis on others. The same results may be obtained by one person as by another, in a different way. It is evident then, that neither one is securing the maximum results. To obtain the correct idea of the relative importance of the different factors, all but one must be kept constant, and this one factor alone varied. The impossible task of keeping the different factors constant, in the practical operation of a plant, makes the practical plant man's experiments of a very doubtful nature. It is perhaps due to this that a part of the difference in opinion, regarding the relative importance of the various factors, has arisen.

To obtain the data presented in this article, the extraction of the chestnut wood was done in a small copper autoclave, heated with steam by means of a steam jacket, and furnished with a

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thermometer and pressure gauge. The temperature could be maintained within narrow limits. The other factors were controlled as stated from time to time.

1. *Influence of the Solvent on the Extraction.*—The only solvent that will be considered in this article, is water. The difference in the quality of the water used in the extraction of chestnut wood, at various places, is very great. It varies from the exceptionally hard water to the one that is alkaline in its reaction. Ed. Nihoul and L. van de Putte*, have shown that the extraction of tanning materials with waters containing salts of the alkaline earths show a decided decrease in yield over extracting the same material with distilled water. This fact is pretty well recognized by extract manufacturers, but the reverse, whether a soft water might still further be improved for extraction by dissolving in it some alkali, has not received so much attention.

2. *Influence of Temperature on the Extraction.*—In an article on chestnut extract by U. J. Thuau[1], he states that, "the extraction is carried on in autoclaves under a pressure of two atmospheres or more, at a temperature up to 130° C. (266° F.). Experiment has shown that the yield of extract increases with pressure up to two atmospheres (121° C.-250° F.), but decreases at higher pressures and temperatures. Above this temperature a part of the tannin decomposes into pyrogallic, gallic and ellagic acids, into pyrocatechin, into anhydrides of tannin, or into glucose." Dumesny and Noyer[2] recommend a temperature of 127° C. (260° F.), and a time of from 15 to 20 minutes for each consecutive decoction of the charge of chips in an autoclave. They consider seven washings sufficient under these conditions, but make no mention of the fineness of the wood used, an all important factor, as will be shown in section 5 of this article.

From the above, and other sources of information, it seems that the French practice in the use of autoclaves for the extraction of chestnut wood is to use a temperature of from 250° to 260° F. and a time of from 15 to 20 minutes for each consecutive

* Communication of the Liege Section of the I. A. L. T. C., November 12, 1903.

[1] J. A. L. C. A., **6**, 36 (1911).

[2] *Wood Products, Distillates and Extracts*, p. 196.

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decoction or washing, of the charge. The practice varies in the United States from the use of temperatures of 230° to 260° F. and a time of from 20 to 30 minutes for each consecutive washing, to the use of as low a temperature as 140° F. for the first decoction and a gradual rise in temperature for each consecutive decoction to about 270° F. for the last, and a time comparable to the above.

For a study of the influence of the temperature of the solvent upon the extraction of chestnut wood, the other five factors were kept constant and the temperature alone was varied. Distilled water at 180° F. was put on the portion of the uniform sample of fresh wood which was to be extracted, and then after each take-off the same amount of water at 180° F. was added. This was a measured amount sufficient to cover the wood. It was then raised to stated temperature in from 5 to 6 minutes and this temperature maintained for the stated time. The resulting liquors were then drawn off and analyzed by the official method of the A. L. C. A., in so far as they could without however, evaporating the very weak ones to bring them to analytical strength.

The wood sample used to arrive at the results shown in tables 1 and 2, was mature wood, chipped and shredded green, sifted thru a ¼" mesh sieve and air dried for three months. The analysis of the wood was:

	Per cent.
Total solids	13.62
Soluble solids	12.88
Non-tannins	3.86
Tannins	9.02
Purity	70.10

A. Constant Temperature Extraction.—The first work was done by the constant temperature method of extraction, in which each new water on the wood is raised to the same temperature, maintained at that temperature for the stated time, and then drawn off. Each portion of wood was washed eight times, this being the number of washings wood receives in the process of extraction with a battery of six autoclaves, where one is in process of being filled while another is being emptied. The grams of tannin and of non-tannin removed by each take-off was cal-

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culated, and from this the purity of the extract which could be made by combining all the take-offs from one portion of wood was determined. The other figures were arrived at in an analogous manner, they are calculated on an absolute dry basis and stated in per cent. The results of this work are shown in Table I.

Referring to the table it will be noticed that the yield in tannin reaches its maximum at a temperature of 270° F. and that the yield at this temperature is practically the same as the laboratory yield. But the surprising fact is that the yield in tannin at this maximum, is only 4.5 per cent. greater than the yield at 210°, while the amount of non-tannin extracted at 270°, as shown by column 5, is more than four times that extracted at 210°, under these conditions of extraction. This small 4.5 per cent. increase in tannin then is obtained at the expense of the very great decrease in purity, 73.6 per cent. to 40.5 per cent. Since both the amount of tannin extracted and the amount remaining in the wood, as shown by analysis, decreases at temperatures above 270° F., we must conclude that part of the tannin is broken up by heat after passing this temperature and under the other conditions of the extraction.

As may be seen in columns 10 and 11, the amount of tannin extracted in the first take-off reaches a minimum at 270° F., while the amount extracted in the last or eighth take-off is at a maximum at the same temperature. It may be inferred from this that near this temperature a part of the most soluble tannin is decomposed, while at the same time a larger portion of difficultly soluble tannin is removed, as indicated by the amount extracted by the last take-off. This at once suggests the idea of the step-up method of extraction, in which the most soluble tannins are removed at a low temperature, and as the extraction proceeds, a higher temperature is used, until finally the last decoction of the wood is made at a comparatively high temperature.

Why so large an amount of tannin is extracted in the first take-offs at the high temperatures of 310° and 330°, and just what quality of tannin this is, will remain as a problem for a future time.

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TABLE I.—CONSTANT TEMPERATURE EXTRACTION.

Column No. 1 No. Take-off	2 Time	3 Temp. F.	4 Purity of the extract Per cent.	5 Non-tannin extra'd Per cent.	6 Tannin extra'd Per cent.	7 Labor-atory extra'n Per cent.	8 Tannin in spent wood Per cent.	9 Purity of spent wood Per cent.	10 Tannin first take-off Grams	11 Tannin in last take-off Grams
8 Take-offs	30 min.	210	73.65	3.110	8.674	9.02	1.64	46.3	9.78	0.586
8 Take-offs	30 min.	230	66.79	4.274	8.590	9.02	0.97	37.7	9.52	0.582
8 Take-offs	30 min.	250	56.16	7.005	8.970	9.02	0.95	31.6	9.52	0.920
8 Take-offs	30 min.	270	40.55	13.28	9.062	9.02	0.79	34.3	7.92	0.935
8 Take-offs	30 min.	290	28.97	20.71	8.450	9.02	0.46	32.1	7.96	0.445
8 Take-offs	30 min.	310	23.60	22.95	7.081	9.02	0.32	32.1	10.20	0.270
8 Take-offs	30 min.	330	20.23	30.25	7.671	9.02	0.31	30.1	13.63	0.207

TABLE II.—STEP-UP METHOD OF EXTRACTION.

Column No. 1 No. Take-off	2 Time	3 Temp. F.	4 Purity of the extract Per cent.	5 Non-Tannin extra'd Per cent.	6 Tannin extra'd Per cent.	7 Labor-atory extra'n Per cent.	8 Tannin in spent wood Per cent.	9 Purity of spent wood Per cent.	10 Tannin first take-off Grams	11 Tannin in last take-off Grams
		150								
8 Take-offs	30 min.	290	57.66	6.91	9.41	9.02	1.42	30.1	3.73	2.44
		170								
8 Take-offs	30 min.	310	43.72	13.20	10.46	9.02	1.20	17.6	5.53	3.24
		190								
8 Take-offs	30 min.	330	36.18	18.51	10.49	9.02	0.95	19.8	6.93	1.26
		210								
7 Take-offs	30 min.	330	36.16	18.63	10.56	9.02	0.91	20.0	7.63	1.07
		230								
6 Take-offs	30 min.	330	36.76	18.12	10.53	9.02	0.99	19.8	8.95	1.64

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B. Step-up Method of Extraction.—For the first work in the step-up method of extraction, a time of 30 minutes for each decoction was chosen, and each succeeding washing after the first was done at a temperature 20° higher that the preceding. Equal portions of the same sample of wood were taken as in the constant temperature work. The results of this work are shown in Table 2.

The first thing to be noted in this table is that the amount of tannin extracted, in every case, is higher than the greatest amount extracted by the constant temperature method. However, with the exception of the one extracted between the temperatures of 150° and 290° F., the purity of the extracts is so low as to inhibit their sale unless at a reduced price. The one extracted at 250° F. by the constant temperature method compares closer in purity to the one extracted between 150° and 290° by the step-up method, the purities being 56.16 per cent. and 57.66 per cent. respectively, while the corresponding yields are 8.97 per cent. and 9.41 per cent. For the next lower corresponding purities, 40.55 per cent. and 43.72 per cent. the yields are by constant temperature method 9.06 per cent. and by step-up method 10.46 per cent. It follows that for the same purity of extract, the step-up method of extraction gives a yield of 5 per cent. to 15 per cent. higher than the constant temperature method, under the conditions of extraction used in making these comparisons. Under less favorable conditions of extraction, the advantage of the step-up method of extraction over the constant temperature method, in this respect, is much more striking. The high amount extracted by the step-up method compared to the amount of tannin extracted by a "Teas' soxhlet" extractor, as shown in column 7, should also be noted. The answer to this greater yield for a corresponding purity may in part be found in the fact that very little of the most soluble tannins are decomposed by exposure to a high temperature, since they are removed in the first one or two take-offs, at a low temperature.

In every case in the step-up method of extraction, the decoction made at a temperature of 290° F., showed more tannin than the preceding decoction made at 270°. This is shown plainly by the yield curves given on page 351. Here is evidence that tannins

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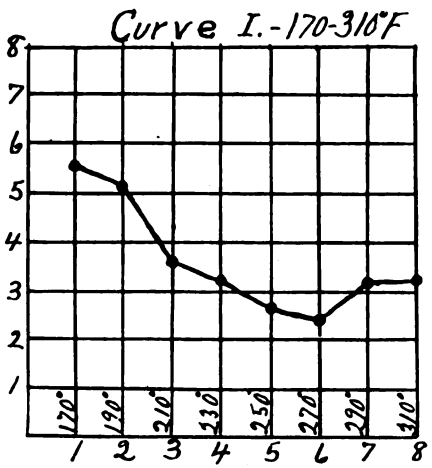
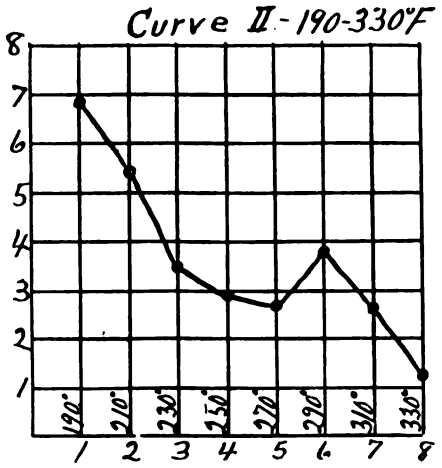
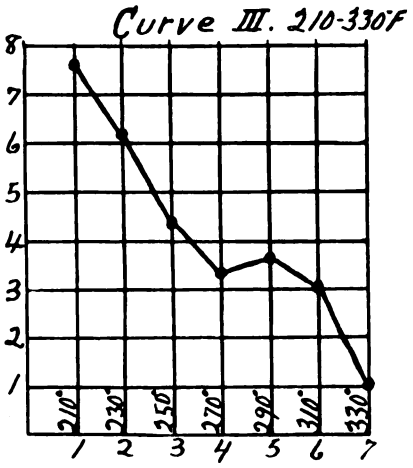
Yield Curves.







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difficultly soluble at 270° F., become much more soluble in water at 290°. This phenomenon is worthy of deeper study.

Table I shows that for short intervals of time a temperature of 270° F. must be passed before appreciable quantities of tannin are decomposed. And by referring to Table III it will be seen that still higher temperatures may be used for very short time periods. The preceding paragraph would indicate that in the step-up method of extraction, to increase the yield it might be advisable to use a temperature even as high as 290° for the last decoction. The amount of tannin removed in the first take-offs, as shown in Tables I and II would lead us to believe that it is needless to use a temperature less than boiling, for the first decoction.

The small increase in the yield of tannin to the comparatively great increase in temperature as in Table I, from 210° to 270° and in Table II from 150-290 to 230-330 may be misleading if we do not consider the fact that the extraction in each case is nearing the point of complete exhaustion. Under less favorable conditions of time and number of take-offs, the great influence of temperature is strikingly shown. To obtain the results presented in Table III, two portions of a uniform sample of wood TT1, chipped, shredded, sifted through an 8-mesh sieve and dried 4 months, were decocted six consecutive times for ten minute periods. It will be seen that 7.89 per cent. tannin was extracted at 210-260° while 8.88 per cent. was extracted at 230-280°, an average temperature only 20° above the first. It follows that for very small periods of time, and few take-offs, a small rise in temperature increases the yield very considerably. Here again it is shown by the very high purity of the extracts, that for small time periods we need not be afraid of a temperature range even considerably higher than the 230-280° range, and we suspect that the decomposition of tannin is decidedly a function of both temperature and time, a problem to be treated more fully at another time.

To learn more definitely the best temperature range to use for the extraction of chestnut wood, three portions of the uniform sample of wood TT1 were extracted under the same conditions except as to range of temperature. The extraction of the first portion was begun at a temperature of 150° F. for each consecu-

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tive decoction a rise in temperature of 20° was effected. Eight decoctions were made, the last at a temperature of 290°. The extraction of the second portion was begun at 210° and finished at 280°, in 10° steps. The extraction of the third portion was effected by decocting four times at 210° and then four times at 270°. The shorter time of 20 minutes for each decoction was chosen in order to prevent the extraction of the wood being so complete as to make comparisons questionable. The results are shown in Table IV. It will be seen here that a range of temperature from 210° to 280° and an increase of 10° for each consecutive decoction has the advantage.

TABLE III.—TTI WOOD, 1/8" MESH.

Column No. 1 No. Take-offs	2 Time	3 Temp. 10° steps	4 Purity of the extract Per cent.	5 Tannin extracted Per cent.
6 Take-offs	10 min.	210 260	75.7	7.89
6 Take-offs	10 min.	230 280	72.1	8.88
6 Take-offs	20 min.	210 260	74.3	7.98
6 Take-offs	20 min.	230 280	69.3	8.91

TABLE IV.—TTI WOOD, 1/8" MESH.

Column No. 1 No. Take-offs	2 Time	3 Temperature	4 Purity of the extract Per cent.	5 Non-Tannin extr'd Per cent.	6 Tannin extr'd Per cent.	7 Laboratory extr'n Per cent.
8 Take-offs	20 min.	150° to 290° by 20° steps	62.4	5.83	9.66	8.27
8 Take-offs	20 min.	210° to 280° by 10° steps	61.4	6.23	9.91	8.27
8 Take-offs	20 min.	4 at 210° 4 at 270°	62.6	5.75	9.64	8.27

3. *Influence of Time on the Extraction.*—A short study of the influence of time on the extraction of chestnut wood, keeping the other five elements that enter into the extraction constant, will do much to point the way to the best combination of the various factors in order to obtain a maximum yield and a high purity.

For the first study, the portions of wood used were chipped green, shredded, passed through a 1/4 inch mesh sieve, and dried three months. A measured volume of distilled water was used for each decoction, just sufficient to cover the portion of wood

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used. Six washings, beginning with a temperature of 210° F. for the first and increasing the temperature 10° for each successive washing, was selected for this comparative study. With six washings the extraction is not carried to completion and more comparative results are obtained. This work is given in Table V. The most interesting thing to note is the rapidly changing

TABLE V.—TTI WOOD, ¼" MESH.

Col. No. 1 No. Take-offs	2 Time	3 Temp. 10° steps Degrees	4 Purity of the extract Per cent.	5 Non-Tannin extra'd Per cent.	6 Tannin extra'd Per cent.	7 Labor-atory extr'n Per cent.	8 Tannin in first take-off Grams	9 Tannin in last take-off Grams
6	15 min.	210 260	70.9	3.22	7.84	8.27	6.09	1.31
6	30 min.	210 260	66.5	4.02	7.99	8.27	5.97	1.35
6	1 hr.	210 260	58.9	5.79	8.32	8.27	6.64	1.52
6	2 hrs.	210 260	52.1	8.33	9.06	8.27	7.04	1.87

ratio between the tannin and the non-tannin extracted as the time for each decoction was increased. This may be summarized as follows:

Amount extracted with 30 minute decoctions over 15 minute decoctions—Tannin, 1.91 per cent.; Non-tannins, 24.85 per cent.

Amount extracted with 1 hour decoctions over 15 minute decoctions—Tannin, 5.88 per cent.; Non-tannins, 80.0 per cent.

Amount extracted with 2 hour decoctions over 15 minute decoctions—Tannin, 15.5 per cent.; Non-tannins, 158.7 per cent.

It will be seen then that under the conditions of these extractions, an increase of time from 15 minute decoctions to 2 hour decoctions, while increasing the yield of tannin 15.5 per cent., at the same time increased the yield of non-tannin 158.7 per cent. No other factor influences the extraction of non-tannin in so great a degree as an increase in the time of decoction under the conditions of autoclave extraction. This makes it highly desirable to use a short time period in autoclave extraction.

To further note the influence of time on the extraction of chestnut wood, four portions of a uniform sample of wood, chipped green on a No. 6 M. & M. chipper but not shredded, and dried one month, were extracted under the same conditions as in Table V. The results are shown in Table VI. It will be seen that with such a coarse preparation a time of two hours for each

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TABLE VI.

Col. No. 1 No. Take-offs	2 Time	3 Temp. 10° steps Degrees	4 Purity of the extract Per cent.	5 Non-Tannin extra'd Per cent.	6 Tannin extra'd Per cent.	7 Laboratory extr'n Per cent.	8 Tannin in first take-off Per cent.	9 Tannin in last take-off Per cent.
6	15 min.	210 260	64.6	3.17	5.80	8.23	4.43	1.66
6	30 min.	210 260	59.6	4.10	6.06	8.23	4.95	1.89
6	1 hr.	210 260	55.5	5.47	6.84	8.23	5.62	2.01
6	2 hrs.	210 260	47.6	9.18	8.33	8.23	7.04	2.81

decoction is necessary, under the conditions imposed, to get a yield equal to the laboratory yield by percolation. At the same time so much non-tannin was extracted as to bring the purity of the extract below practical limits. The amount of tannin extracted with two hour decoctions over 15 minute decoctions in the case of this coarse preparation is 43.6 per cent. as against the 15.5 per cent. in the case of the finer preparation used to obtain the results in Table V. This is a strong argument in favor of a fine preparation and the strength of the argument will be more fully dealt with in Section 5 of this article.

As a means of studying the time element under the conditions of open leach extraction three portions of a uniform sample of wood, the same as the sample used to obtain the results in Table VI, were decocted nine times at a temperature of 210° F. A measured volume of distilled water just sufficient to cover the portion of wood was used for each decoction. The results are summarized in Table VII.

TABLE VII.

Col. No. 1 No. Take-offs	2 Time	3 Temp. Degrees	4 Purity of the extract Per cent.	5 Non-Tannin extra'd Per cent.	6 Tannin extra'd Per cent.	7 Laboratory extr'n Per cent.
9	30 min.	210	69.2	2.84	6.39	8.23
9	1 hr.	210	68.0	3.21	6.83	8.23
9	2 hrs.	210	66.3	3.95	7.76	8.23

It will be seen here that the purity of the extract is not greatly affected by the increase in the time of decoction. Another point is that nine decoctions of two hours each, a total of 18 hours, is not sufficient to extract as much tannin as was extracted by percolation in the laboratory. Comparing these results with the results obtained under the conditions of open leach extraction

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shown in Table I, it would seem that a fine preparation is also desirable where the open leach method of extraction is in use.

Following the idea that a fine preparation of wood ought to be extracted in a very short time, six portions of a uniform sample of wood TT1, ground green, shredded, dried 6 months, and sifted through a 1/8" mesh sieve, were decocted the time and temperatures shown in Tables VIII and IX.

TABLE VIII.—TT1 Wood, 1/8" Mesh.

Col. No. 1 No. Take-offs	2 Time	3 Temp. 10° steps Degrees	4 Purity of the extract Per cent.	5 Non-Tannnin extra'd Per cent.	6 Tannin extra'd Per cent.	7 Labor-atory extr'n Per cent.
6	10 min.	210 260	75.7	2.54	7.89	8.27
6	20 min.	210 260	74.3	2.76	7.98	8.27
6	30 min.	210 260	71.0	3.33	8.16	8.27

TABLE IX.—TT1 Wood, 1/8" Mesh.

Col. No. 1 No. Take-offs	2 Time	3 Temp. 10° steps Degrees	4 Purity of the extract Per cent.	5 Non-Tannin extra'd Per cent.	6 Tannin extra'd Per cent.	7 Labor-atory extr'n Per cent.
6	10 min.	230 280	72.1	3.44	8.88	8.27
6	20 min.	230 280	69.3	3.94	8.91	8.27
6	30 min.	230 280	65.4	5.02	9.47	8.27

The results speak for themselves, yet one cannot refrain from commenting on the remarkably high purities and high yields shown in Table IX, when we take into consideration the high temperature used for the consecutive decoctions. It would seem that the conditions imposed upon the preparation and extraction of the wood to obtain the results shown in Table IX are approaching something near the ideal conditions for autoclave extraction. There remain, however, three other elements in the extraction of wood to be studied before drawing conclusions.

4. *Influence of the Ratio of Solvent to Wood on the Extraction.*—For a comparison of the influence of the ratio of the amount of water to the amount of wood used for extraction, a temperature range of from 210° to 260° F. in 10° steps, a time of 30 min. for each decoction and six decoctions, were chosen for the first comparisons. Four portions of a uniform sample of wood,

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chipped, shredded, sifted through a ¼" mesh sieve and dried two months, were extracted. For the same amount of wood (300 grams) 1000 cc., 1333 cc., 2000 cc., and 4000 cc., of water were used for the decoctions. 1000 cc. is sufficient to cover the wood and is a normal extraction. The results are given in Table X.

TABLE X.—TTI WOOD, ¼" MESH.

Col. No. 1 No. Take-offs	2 Amt. water for each decoction	3 Grams wood used	4 Time	5 Temp. 10° steps Degrees	6 Purity of the extract Per cent.	7 Non-Tannin extra'd Per cent.	8 Tannin extra'd Per cent.	9 Laboratory extr'n Per cent.
6	1,000 cc.	300	30 min.	210 260	67.2	4.22	8.64	8.27
6	1,333 cc.	300	30 min.	210 260	67.4	4.27	8.78	8.27
6	2,000 cc.	300	30 min.	210 260	66.4	4.50	8.86	8.27
6	4,000 cc.	300	30 min.	210 260	67.5	4.41	9.17	8.27

Here it will be seen that regardless of the amount of water used for each decoction, the purity of the extracts is remarkably constant, as may also be seen in Table XI. The difference in the amount of tannin extracted with only sufficient water to cover the wood, 1000 cc., and the amount extracted with four times this much water is relatively small, being only 6.13 per cent. of the amount extracted using 1000 cc. for each decoction. Believing that such a small difference in tannin extracted may in part be due to the fact that the 8.64 per cent. extracted with sufficient water to cover the wood, is perhaps approaching complete extraction, a series of three other extractions were made under less favorable conditions as regards time and the amount of water used. This work is shown in Table XI.

TABLE XI.—TTI WOOD, ⅛" MESH.

Col. No. 1 No. Take offs	2 Amt. water for each decoction	3 Grams wood used	4 Time	5 Temp. 10° steps Degrees	6 Purity of the extract Per cent.	7 Non-Tannin extra'd Per cent.	8 Tannin extra'd Per cent.	9 Laboratory extr'n Per cent.
6	450 cc.	300	15 min.	210 260	77.3	1.86	6.34	8.27
6	900 cc.	300	15 min.	210 260	75.8	2.72	8.53	8.27
6	1,800 cc.	300	15 min.	210 260	74.9	3.05	9.18	8.27
*10	450 cc.	300	10 min.	230 275	71.6	3.27	8.25	8.27

* Five steps.

The wood used was the same as in Table X except it was sifted through a ⅛" mesh screen. Three hundred grams of

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wood were used each time. It required only 900 cc. of water to cover the wood, as against the 1000 cc. required to cover 300 g. of the coarser preparation. Where the amount of water used for each decoction is shown to be 450 cc., 900 cc., of water was placed on the wood but only half this amount was drawn off at each take-off, and this amount was then replaced with distilled water for the next decoction. The difference in tannin extracted with 900 cc. and 1800 cc. of water is again small, being 7.52 per cent. of that extracted with 900 cc. But when the amount of liquor drawn at each take-off is cut to 450 cc., the time, temperature, and other conditions remaining the same, the tannin yield drops from 8.53 per cent. to 6.34 per cent. This decrease in yield may however be remedied by drawing a sufficient number of take-offs. This may be seen in the last line of the table, where the results of 10 take-offs of 450 cc. each, with a time for each of 10 minutes, and a temperature range of from 230° to 275° F. in 5° steps is shown.

5. *Influence of Preparation on the Extraction.*—It is universally recognized that a fine preparation of raw tanning materials is necessary for a rapid extraction. Not only should the chestnut extract manufacturer recognize that a fine preparation is essential to rapid and complete extraction, but he should also gain an idea as to just what part the chipping and what part the shredding of the wood has to do with the quality of the preparation. The experiments made to procure the following data were made with this end in view as well as to emphasize the importance of a fine preparation for rapid extraction.

The conditions of the experiments were chosen so that a yield approaching the practical limit would be obtained from the portion of finest preparation, while from the coarser preparations a corresponding decrease in yield would be expected. Thirty minutes for each digestion and six washings, the first at 210°, the second at 220°, etc., to 260° F., were chosen. The portions of wood used were all cut from the same stick of wood, the entire cross section of the wood being used for each portion. The wood was young, green wood, dried four months. The results of the work are shown in Table XII.

By examining column 4 of the table, it will be seen that the highest purity extract was obtained from the finest preparation,

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TABLE XII.

Column No. 1 Preparation	2 No. Take-offs	3 Temp. 10° steps Degrees	4 Purity of the extract Per cent.	5 Tannin extra'd Per cent.	6 Tannin first take-off Grams	7 Tannin last take-off Grams
Sawdust	6	210 260	66.6	7.11	5.86	0.896
¼″ Cubes	6	210 260	63.80	5.52	3.08	1.85
½″ Cubes	6	210 260	63.80	3.86	1.76	1.70
⅛″ Sq. cross section area ½″ along the length of grain	6	210 260	62.81	4.73	3.28	1.40
1″ Cubes	6	210 260	61.43	2.44	1.00	1.20
¼″ Sq. cross section area 1″ along the length of grain	6	210 260	59.65	3.14	1.58	1.47
1″ Sq. cross section area ¼″ along the length of grain	6	210 260	63.99	5.09	2.71	1.87

as was also the greatest yield. This fact ought to be gratifying to the extract manufacturer. The probable explanation may lie in the fact that tannin is more easily extracted than non-tannin. The tannin from the surface of the piece of wood is quickly removed, the non-tannin less quickly. Then under further extraction non-tannin continues to be removed from the surface of the piece of wood to a greater extent than the tannin, while the same proportion of tannin and non-tannin as was removed from the surface, are removed from further within the piece of wood.

Regarding the influence of splitting or shredding, and cutting across the grain, we obtain the following ratios from the table:

Ratio of areas of pieces ¼″ sq. cross section and 1″ grain length, to ¼″ cubes, per gram of wood, is 1 to 1.33.

Ratio of yield of pieces ¼″ sq. cross section and 1″ grain length, to ¼″ cubes, per gram of wood, is 1 to 1.76.

Ratio of area of ½″ cubes to pieces ⅛″ sq. cross section and ½″ grain length, per gram of wood, is 1 to 3.

Ratio of yield from ½″ cubes to pieces ⅛″ sq. cross section and ½″ grain length, per gram of wood, is 1 to 1.226.

Ratio of area of 1″ cubes to pieces ¼″ sq. cross section and 1″ grain length, per gram of wood, is 1 to 3.

Ratio of yield from 1″ cubes to pieces ¼″ sq. cross section and 1″ grain length, per gram of wood, is 1 to 1.288.

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Ratio of area of 1" cubes to pieces 1" sq. cross section and ¼" grain length, per gram of wood, is 1 to 2.

Ratio of yield from 1" cubes to pieces 1" sq. cross section and ¼" grain length, per gram of wood, 1 to 2.088.

We may see from these ratios that in general, under the conditions of the experiments, tripling the area by splitting or shredding increased the yield about 25 per cent. while doubling the area by cutting across the grain, or chipping, increased the yield about 100 per cent.

The shredder or pulverizer as used in extract plants must not however be condemned at once by these results, for it will be remembered that the chips in passing through the shredder may not only have their area tripled by splitting, but may have it increased 5 or 6 times, and at the same time a great deal of breaking across the grain always occurs. There is a point, as shown by the table, decidedly in favor of shredding. By examining column 6 we see that in extracting ½" cubes, 1.76 grams was removed in the first take-off, while in extracting pieces with a ⅛" cross section area and ½" grain length, 3.28 grams of tannin were removed in the first take-off. This is almost double the amount of the former first take-off, while the yield ratio is as 1 to 1.23. And again, in extracting 1" cubes, 1 gram was removed in the first take-off, while from pieces ¼" cross section area and 1" grain length, 1.58 grams tannin were removed in the first take-off. This is proof that the surface exposed by splitting is a surface from which the tannin is very readily and rapidly extracted. Very fine shredding then will be necessary for the most rapid extraction.

6. *Influence of the Number of Washings, Take-offs or Decoctions, on the Extraction.*—It was found by experiment that for a preparation of wood sifted through a ¼" mesh sieve, the volume of water retained by the wood and the volume of water drawn off when the wood was just covered, were as 8 to 9. Then if we were to assume that the tannin in the wood was all dissolved in a short period of time, we could expect to get about ½ the tannin out of the wood the first washing, ½ of that remaining the second washing, etc. After 6 washings there would be but 1/64 of the original amount of tannin, remaining in the wood. This would be near enough to the complete exhaustion of the

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wood. That these assumed conditions are far from being the true conditions in the extraction of wood will be seen readily by referring to tables XIII and XIV.

TABLE XIII.—AA1 Wood.

Analyses of Eight Consecutive Take-offs.

The take-off	Time	Temp. Degrees	T. S.	S. S.	Ins.	N. T.	T.	Purity Per cent.	Grams of tannin
1st	30 min.	230	1.59	1.50	0.09	0.38	1.12	70.6	9.520
2nd	30 min.	230	0.96	0.91	0.05	0.28	0.63	65.7	5.922
3rd	30 min.	230	0.54	0.49	0.05	0.17	0.32	59.3	3.040
4th	30 min.	230	0.42	0.32	0.10	0.12	0.20	47.6	1.940
5th	30 min.	230	0.28	0.23	0.05	0.10	0.13	46.4	1.261
6th	30 min.	230	0.23	0.20	0.03	0.09	0.11	45.3	1.078
7th	30 min.	230	0.19	0.15	0.04	0.08	0.07	39.4	0.686
8th	30 min.	230	0.16	0.13	0.03	0.07	0.06	39.3	0.582
								Total	24.029

TABLE XIV.—TT1 Wood.

Analyses of Six Consecutive Take-offs.

The take-off	Time	Temp. Degrees	T. S.	S. S.	Ins.	N. T.	T.	Purity Per cent.	Grams of tannin
1st	15 min.	210	1.005	0.956	0.049	0.213	0.746	77.8	6.093
2nd	15 min.	220	0.700	0.651	0.049	0.168	0.483	74.2	4.444
3rd	15 min.	230	0.499	0.456	0.043	0.122	0.334	73.3	3.223
4th	15 min.	240	0.363	0.310	0.053	0.097	0.213	68.7	2.087
5th	15 min.	250	0.313	0.267	0.046	0.106	0.161	60.3	1.546
6th	15 min.	260	0.325	0.267	0.038	0.130	0.137	51.3	1.308
								Total	18.701

In table XIII it is shown that about 1/40 of the total amount of tannin extracted was extracted in the last or 8th take-off, and we may consider this to be approaching the practical limit of extraction under the imposed conditions. In table XIV about 1/15th of the total amount of tannin extracted was extracted in the last or 6th take-off, and this amount is about 1/5th of that removed in the first take-off. In this case the practical limit of extraction has certainly not been reached, and if the practical limit of extraction is to be reached under these conditions, the wood will have to be subjected to a greater number of decoctions.

From the grams of tannin removed in the consecutive take-offs as shown in tables XIII and XIV, the curves No. 1 and No. 3 page 362 were plotted. Curve No. 2 was plotted from a table

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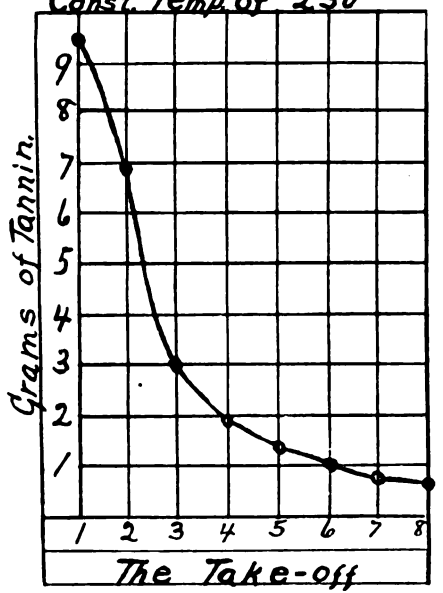
Yield Curves:

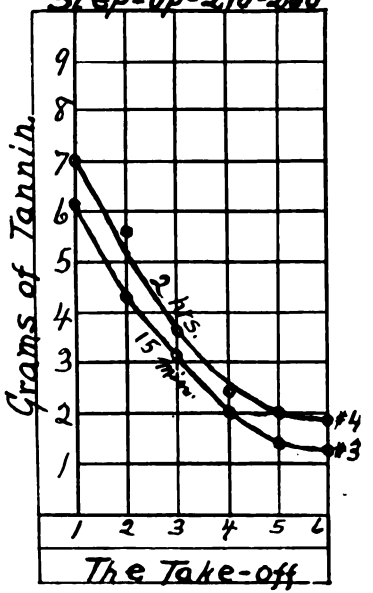
#1

Const. Temp. of 230°



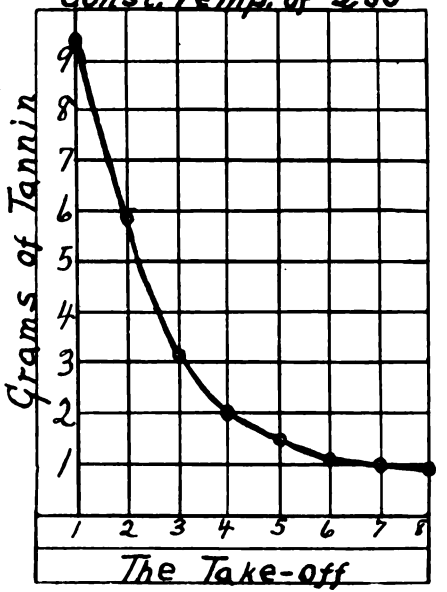
#3 and 4.

Step-up-210°-260°



#2

Const. Temp. of 250°



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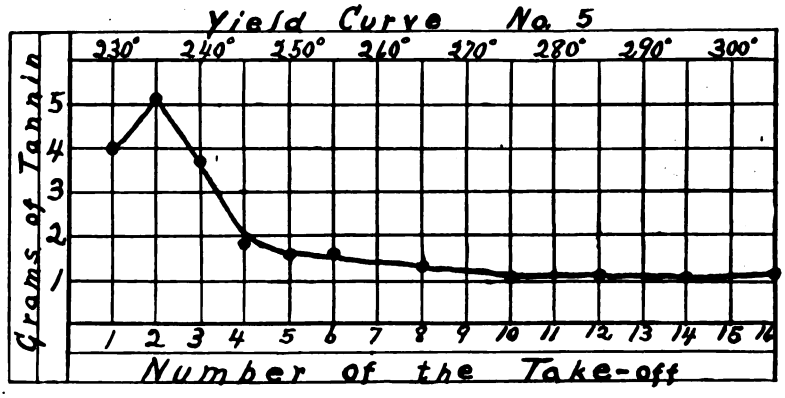
similar to No. 13 except that the temperature of extraction was 250°, and curve No. 4 was plotted from a table similar to No. 14 except that the time of extraction was 2 hours instead of 15 minutes for each decoction. Curves No. 1 and No. 2, especially, take somewhat the form of exponential curves, and show that with the constant temperature method of extraction complete exhaustion of the wood could not be reached, and that the individual operator must choose a practical limit to the number of decoctions. Curves No. 3 and No. 4 show very clearly that increasing the time for each decoction from 15 minutes to 2 hours, is not a substitute for increasing the number of decoctions, but that in either case the wood should have been subjected to a greater number of decoctions.



Bringing the conditions of extraction as near as possible to the actual operating conditions of a battery of autoclaves by removing 450 cc. of liquor in each take-off, as in lines 1 and 4 of table XI, choosing a time period of 10 minutes for each decoction, and a temperature range beginning at 230° F. and increasing 5° for each consecutive take-off, a more definite idea will be obtained as to the number of washings required in the extraction of chestnut wood. Curve No. 5 is the yield curve for 16 consecutive take-offs made under the above conditions. The wood used was the same as that used to obtain the results in table XI and was an ⅛" mesh preparation.

It will at once be seen that with this short time period and slow increase in temperature, a great number of washings is apparently

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necessary for anything like complete extraction. Then in choosing the proper number of washings one must not be governed by the yield curve alone but also by the purity of the product. The calculated purity of the combined extractives removed in 12 take-offs is 66.5 per cent., while after this point is passed, the purity rapidly drops below the practical limit. The yield for 12 take-offs is 9.04 per cent. from a wood which the highest of three laboratory analyses showed to contain 8.27 per cent. tannin. Under the above conditions, which approach very closely to the ideal in regard to time, temperature, preparation, and amount of water used, it would seem inadvisable to subject the wood to more than 12 or 14 washings. Twelve is the number of washings to which a wood is subjected with a battery of 8 autoclaves under normal operating conditions.

It is shown in section 2 that the step-up method of extraction is productive of the greatest yield of extract, at a certain purity, or in other words, for the same yield, the extract produced by the step-up method of extraction will have the highest purity. It is shown that a temperature range of 210-300° F. is permissible when short intervals of time are used for each decoction.

In section 3 it was seen that under the conditions of high temperature, autoclave extraction, an increase in the period of time for each decoction increased the amount of non-tannin very greatly, and consequently when high temperatures are used a small interval of time is absolutely necessary to obtain a high purity extract, while in the open leach method of extraction a long period of time may be used without affecting the purity of the extract to any considerable extent. It is also seen that a ten minute interval may be sufficient for each decoction, provided that a high enough temperature and a fine enough preparation of wood are used.

In section 4 it was pointed out that the amount of water used for each decoction affected the purity very little; that using an amount of water for each decoction from twice to four times the amount sufficient to cover the wood, "washed out" only a small additional quantity of tannin, but that when less than this amount was removed in each take-off, the yield in tannin rapidly decreased. From this it follows that in the practical operation of a battery of autoclaves few in number, say six, the small

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number of washings the wood is subjected to may be compensated for by removing a greater volume of water for each take-off. This will tend to have the same effect as using pure water for each consecutive decoction.

The work shown in section 5 was evidence of the importance of a fine preparation, and that a wood finely shredded is capable of a very rapid extraction.

It was shown in section 6 that increasing the time and temperature is no proper substitute for a greater number of decoctions and that 12 is about the minimum number of washings to which chestnut wood should be subjected in the practical operation of autoclaves.

In an attempt to combine what was concluded to be the best conditions of the various factors in the extraction of chestnut wood, a 300 gram portion of TT1 wood, ground green, shredded, dried 6 months, and sifted through a 1/8" mesh sieve, was decocted 16 times by placing 900 cc. water on the wood, and after drawing off 450 cc. for a take-off, replacing it each time with the same amount. A ten minute period for each decoction, and a range of temperature beginning at 230° F. for the first decoction and increasing this temperature 5° for each consecutive decoction, was used. The ratio of water to wood parallels very closely the ratio of water to wood used in a six autoclave battery, when 1400 gallons of water per cord (160 cu. ft.) of wood are drawn from the head autoclave. The purity of the liquors and grams of tannin extracted each take-off are shown in table XV.

For ten take-offs it will be seen that the purity of the combined extractives is 71.62 per cent. and the tannin extracted is 8.25 per cent. The laboratory analysis of the wood showed a purity of 70.3 per cent. and 8.27 per cent. tannin. The difference in time for these equal extractions is the difference between 100 minutes for the autoclave extraction, and 16 hours for the percolation extraction. The percolation extraction also had the advantage of a 20 mesh to the inch preparation. For twelve take-offs the purity is still excellent and the yield in tannin is 9.04 per cent. or about 8.36 per cent. more than the laboratory yield. The high yield in tannin for the 16 take-offs, 10.76 per cent. is a surprisingly high yield for a wood which analyzes only 8.27 per cent. tannin, as the highest of three different analyses,

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and is a yield that cannot be obtained by the open leach method of extraction.

TABLE XV.—300 GRAMS OF TTI WOOD, 1/8" MESH.

Number of take-off	Time	Temp.	Amount of take-off	Purity	Grams of tannin
1st	10 min.	230	450 cc.	79.2	4.002
2nd	10 min.	235	450 cc.	80.4	5.170
3rd	10 min.	240	450 cc.	78.1	3.676
4th	10 min.	245	450 cc.	75.1	1.942
5th	10 min.	250	450 cc.	71.1	1.798
6th	10 min.	255	450 cc.	67.1	1.380
7th	10 min.	260	450 cc.	64.4	1.304
8th	10 min.	265	450 cc.	60.2	1.242
9th	10 min.	270	450 cc.	55.1	1.073
10th	10 min.	275	450 cc.	45.5	0.987
11th	10 min.	280	450 cc.	41.1	1.114
12th	10 min.	285	450 cc.	37.0	1.136
13th	10 min.	290	450 cc.	34.7	1.121
14th	10 min.	295	450 cc.	28.3	1.082
15th	10 min.	300	450 cc.	26.4	1.117
16th	10 min.	305	450 cc.	24.4	1.303

For 8 Take-offs—N. T. = 6.902 grams; Purity = 74.8 per cent.; Tannin = 7.50 per cent.
For 10 Take-offs—N. T. = 8.945 grams; Purity = 71.6 per cent.; Tannin = 8.25 per cent.
For 12 Take-offs—N. T. = 12.46 grams; Purity = 66.5 per cent.; Tannin = 9.04 per cent.
For 14 Take-offs—N. T. = 17.25 grams; Purity = 60.9 per cent.; Tannin = 9.84 per cent.
For 16 Take-offs—N. T. = 24.39 grams; Purity = 54.7 per cent.; Tannin = 10.76 per cent.

In practice, 12 washings of chestnut wood may be secured with a battery of 8 tall autoclaves, operated by the press-over system and designed to withstand a working pressure of about 125 pounds. By the use of autoclaves, tiling lined the proper thickness, and covered externally with insulating material, the proper temperature fall between the tail and head autoclave will be maintained automatically. The temperature of the water entering the tail autoclave is easily regulated where one or more boilers are set aside for heating the water. If an autoclave of a battery is filled every twenty minutes, the average time for each washing will be regulated to 10 minutes, while the ratio of water

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to wood is easily regulated by the amount of liquor removed from each new head autoclave. As to preparation, in a plant where there is already installed a chipper and shredder, a preparation of a fineness corresponding to 5 or to 6 mesh to the inch may be prepared readily by the addition of the proper screening capacity, and a small fine meshed pulverizer of the swing-hammer type. Both the large and small shredding machines should be protected by suitable electro-magnets.

RICHWOOD, WEST VA.

ON THE VOLUMETRIC DETERMINATION OF CHROMIUM IN CHROME LEATHER.

By Te-Pang Hou.

Rec'd. May 4, 1920

As chrome tannage is gaining its headway with such tremendous strides nowadays, the determination of the percentage of Cr_2O_3 a given leather contains should be of great importance both to the tanners and leather chemists. The volumetric determination of chromium as chromate against $Na_2S_2O_3$ solution using KI and starch is a rapid and accurate one and deserves its popularity among leather analysts. Any precaution, then, in connection with the mode of procedure condusive to correct results deserves the consideration of leather analysts.

The writer, in carrying out his research work along other aspects of the tanning industry, was side-tracked by this analytical side of leather analysis. He found that the figure for chromium as determined by this volumetric method when the ash of the leather was fused with a mixture of K_2CO_3, Na_2CO_3 and $Na_2B_4O_7$ did not agree with that obtained by the same method when the chromic salt solution obtained from the same sample was oxidized with Na_2O_2 added to the solution. The discrepancy was too large to be accounted for by the uniform character of the sample. He noticed also that in the latter case the end point as shown by the discharge of starch blue color was not permanent, but returned repeatedly after a lapse of a few seconds each time. It might be added here that in carrying out the determination he closely followed the usual direction for chrome determination as given in the leather laboratory manual in regard to boiling to

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decompose Na_2O_2 in the solution.[1] In view of the seriousness of the situation he was led to investigate the matter.

A ready and handy suggestion naturally would be that the phenomenon might have its origin in the insufficient amount of the acid present in the solution. But further investigation revealed that this was not the case here and over 5 cc. excess of concentrated hydrochloric acid had been added. After elimination of different factors that supposedly might give rise to the trouble, he traced the cause to the presence of a small amount of H_2O_2 (from Na_2O_2 left undecomposed) in the solution.

With this clue on hand he set out to study the behavior further. He found that when Na_2O_2 was left in a solution (vol. 150-200 cc.) to the amount of 12½ mg., the color of the starch blue was discharged and soon returned as often as twenty-six times during the titration. The interval between the discharge of the starch blue color and its reappearance, in the majority of cases, varied between five seconds and thirty-five seconds. For a few readings toward the end of titration it took from one minute to four or five minutes for the color to come back. Finally, a permanent end point was reached which corresponded to the theoretical amount of Na_2O_2 present. The color of the solution as the starch blue color cleared away was greenish—the color of Cr^{+++} salt in dilute solution.

A pure $K_2Cr_2O_7$ solution known to be free from any peroxide was taken and the behavior studied, using the same amount of the acid. The end point was discharged sharply and the starch blue color did not return even after standing for two hours. A violet to blue color appeared, however, after standing longer, or overnight; but that was found to be due to an entirely different cause. It was found that the return of the color after standing for a number of hours or overnight was due to the oxidation of HI, probably with the aid of light, by the oxygen of the air liberating a small amount of iodine. For, if the solution is kept in the dark, a comparatively slight amount of color was observed. When the air was excluded from the flask, absolutely no color was observed after forty-eight hours even when the solution was

[1] Compare, however, *Leather Trades Chemistry*, by S. R. Trotman, (1908) Ed., p. 172, and *Leather Industries Laboratory Book*, by H. R. Procter, Second Ed., p. 262.

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exposed to bright daylight. This was carried out by placing the solution in an Erlenmeyer flask, bringing it to a boil, adding starch, immediately stoppering the flask, and cautiously immersing the mouth under water; when a vacuum resulted above the solution.

Next, a pure dichromate solution with an insufficient amount of the acid (HCl) present was studied. Similar phenomenon of the blue color being discharged and returning was observed, but with a distinct difference. For, in the first place, when the phenomenon was due to insufficient acidity, no appreciable amount of I_2 was liberated upon the addition of KI; and, in the second place, during the course of titration when the starch blue color was discharged, the color of the solution, thus revealed, was yellow or greenish yellow, instead of greenish white. This difference affords a crude diagnosis.

The following quantitative study in regard to acidity in the solution was made and the results tabulated: 0.2000 g. of pure and dried $K_2Cr_2O_7$ was dissolved and made up to 500 cc. volume, 50 cc. of which were taken for each experiment. In each case after adding the desired amount of acid, 5 cc. of KI solution (10 g. KI : 100 cc. water) and 1 cc. starch (½ g. starch : 100 cc. water) were used. The time after addition of KI and before titration was started was about six to eight minutes.

From the above results it follows that when the acidity of 1.00 cc. concentrated HCl (N= 10.72) in about 57 cc. of the solution (50 cc. solution + 1 cc. HCl + 5 cc. KI + 1 cc. starch solution) is attained, titration will go to completion before the starch blue color is discharged: *i. e.*, the rate of I_2 liberated from HI by the dichromate is sufficiently great to replenish the removal of I_2 by $Na_2S_2O_3$. This corresponds to a degree of acidity of 0.18 — 0.19 moles HCl per liter. As the change in the effect of H^+ ion concentration is gradual and as the result is dependent upon the rate of running in the sodium thiosulphate solution, it would be rather impracticable to establish a fast boundary for the acid concentration below which the titration cannot proceed without the blue color of the starch being discharged before the end point is reached. But the above concentration of 0.18-0.19 moles HCl per liter represents a good working minimum.

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ON VOLUMETRIC DETERMINATION OF CHROMIUM IN CHROME LEATHER.

No.	cc. Conc. HCl added (N = 10.72) cc.	Obs. color upon addition of KI	Obs. color upon addition of starch	cc. $Na_2S_2O_3$ (N = 0.04843) Taken before blue color was 1st discharged cc.	Color of solution after starch blue color was 1st discharged	Time taken before blue color returned	Obs. color change after standing overnight	Theoretical amount of 0.04843 N $Na_2S_2O_3$ calculated from $K_2Cr_2O_7$ taken cc.
1	0.00	No change	No. (1) chauge	——	(Yellow color from start)	——	Olive green particles suspended throughout solution.	8.43
2	0.20	Slightly red Deepens slowly	Blue	6.87	Yellow	2–3 min. (olive green)	Olive green particles settling at bottom with solution yellow	8.43
3	0.50	Red slowly	Blue	8.01	Greenish Yellow	2–3 min. (blue)	Olive green particles settling at bottom with solution light yellow.	8.43
4	1.00	Red immediately	Blue	8.42	Greenish white	Violet color barely noticed after 2 hrs.	Violet coloration throughout.	8.43

(1) Slight olive green color appeared on surface after one-half hour.

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ON VOLUMETRIC DETERMINATION OF CHROMIUM IN CHROME LEATHER.—(Continued)

No.	cc. Conc. HCl added (N = 10.72) cc.	Obs. color upon addition of KI	Obs. color upon addition of starch	cc. $Na_2S_2O_3$ (N = 0.04843) Taken before blue color was 1st discharged cc.	Color of solution after starch blue color was 1st discharged	Time taken before blue color returned	Obs. color change after standing overnight	Theoretical amount of 0.04843 N $Na_2S_2O_3$ calculated from $K_2Cr_2O_7$ taken cc.
5	2.00	Red immediately	Blue	8.43	Greenish white	No change within 2 hours	Violet coloration throughout but deeper than (4)	8.43
6	3.00	Red immediately	Blue	8.44	Greenish white	No change within 2 hours	Olive green particles settling at bottom with solution light yellow	8.43

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The return of color, especially in *(6)* after standing over night, in such an abundant way compared with *(5)* or *(4)*, and also in *(5)* noticeably greater than in *(4)*, cannot be readily accounted for, unless the high acid concentration in *(6)*—3 cc. concentrated HCl in original 50 cc. solution—also has the effect of increasing the rate of oxidation of I^- to I_2 by the oxygen from the air. The writer, however, does not like to draw a definite conclusion, as the data here are not sufficient, and to determine definitely would require further study.

From the above phenomena the oxidation by a dichromate would not be adequately expressed simply by

$$Cr^{VI} \rightarrowtail Cr^{III}$$

but rather by

$$Cr_2O_7^{=} + 14H^+ \rightarrowtail 2Cr^{III} + 7H_2O$$

since H^+ ion concentration is a factor in bringing about the change. From this it is clear that the oxidation potential of a dichromate solution is expressed by

$$E \text{ (Oxid. Pot.)} = \frac{4.19\ RT}{6 \times 96504} \log_e \frac{C_{Cr_2O_7^{=}} \times C_{H^+}^{14}}{C_{Cr\,III}^{2}} \times K \text{ volts}^3$$

Where R is in calories, 6 is the loss of number of positive charges, $Cr_2O_7^{=} \rightarrowtail 2Cr$, K is an equilibrium constant characteristic of the oxidizing agent in the reaction and C's with subscripts are molal concentrations per liter for the respective ions. The other figures and symbols are sufficiently obvious.

$$= \frac{0.580}{6} \log_{10} \frac{C_{Cr_2O_7^{=}} \times C_{H^+}^{14}}{C_{Cr^{III}}^{2}} \times K \text{ volts}^3 \text{ at } 20^\circ \text{ C.}$$

As the H^+ concentration in the above expression is to be raised to the fourteenth power we can readily understand why the degree of acidity in the solution plays such an important role in the reaction.

In the case where the excess of Na_2O_2 is incompletely decomposed by boiling when the volume of the solution is large, the reactions are:

$$H_2O_2 + 2HI \rightarrowtail I_2 + 2H_2O \ldots\ldots\ldots\ldots (1)$$ (after addition of acid)

$$I_2 + 2Na_2S_2O_3 \rightarrowtail 2NaI + Na_2S_4O_6 \ldots (2)$$

[3] See Bredig, *Zeit. f. Elektro-Chemie*, 4, p. 544 (1897).

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The reaction (1) is comparatively slow and takes time,[4] while reaction (2) is very rapid. Hence the progress of the two reactions combined is controlled by reaction (1). Now $I_2 \rightarrow 2I^-$ and $O_2^- \rightarrow 2O^=$ have electromotive forces not very far from each other, the first being 0.345 (against normal calomel electrode) and the second 0.110.[5] This may help us to see why the displacement of I^- by $O^=$ in the reaction (1) is so slow, although the oxygen from H_2O_2 will have different amount of free energy than the oxygen from the gaseous state. The discharge of the starch blue color before the final end point is reached simply means that the rate of removal of I_2 by $Na_2S_2O_3$ is faster than that with which it can be supplied from reaction (1). After we stop adding $Na_2S_2O_8$ for a few seconds, of course some iodine is liberated which goes to color the starch again. Hence, the color returns after a lapse of a few seconds or more.

From the above investigation mere boiling would not always suffice to decompose all the excess of the Na_2O_2 used, especially when the bulk of the solution is large, say 200-300 cc. In giving out directions for the chrome determination in leather the writer would direct the solution after oxidation with Na_2O_2 to be gently evaporated down to a small volume, 10 to 15 cc. (repeating if necessary by replenishing the water), then dilute it back for titration. 5 to 10 cc. of the excess of concentrated HCl over the amount necessary to convert the $CrO_4^=$ to $Cr_2O_7^=$ should be present when the bulk of the solution to be titrated is 150-250 cc. (depending also upon the amount of chromium present). In all cases it is wise not to take too large an excess of Na_2O_2 for oxidation. If the acidity is sufficiently high and if the blue color is found to be discharged and come back within a few seconds,

[3] The value of K was estimated to be roughly 10^{17} by Dr. H. A. Fales, Columbia Univ., basing his calculation on the equilibrium constant for $I_2 \rightarrow 2^-$, Maitland, *Zeit. f. Electrochemie*, Vol. 12, p. 268 (1906), and the data given by Loimaranta, *Zeit. f. Electrochemie*, Vol. 13, p. 34 (1907) for the dichromate.

[4] See *Analytical Chem.*, Vol. II, by F. P. Treadwell, translated by Hall. 1919 Ed., p. 680, directing the solution to stand for 5 min. before titration.

[5] See Lewis, *A System of Physical Chemistry*, Vol. II, Second Ed., p. 165, and Le Blanc, *Textbook of Electro-Chemistry*, translated by Whitney and Brown (1907), p. 248.

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some Na_2O_2 is very properly left undecomposed, and the result should be rejected.

With the above precautions the iodimetric determination of chromium is rapid, the end point is very sharp, and definite; and the method possesses a high degree of accuracy.

The writer is under constant obligation to Professor D. D. Jackson, Columbia University, and Dr. Allen Rogers, Pratt Institute, for the interest they have taken in following the work.

COLUMBIA UNIVERSITY.

VEGETABLE TANNING AS A COLLOID-CHEMICAL PROCESS.*

By John Arthur Wilson.

Rec'd May 6, 1920

Preliminary to tanning, a hide is freed from hair, epidermis, and adipose tissue, leaving only the corium, which consists chiefly of bundles of collagen fibers. The prepared hide is then hung in a very weak solution of the tanning material and moved to a stronger liquor each day or two until completely tanned. Vegetable tanning, then, is simply the reaction taking place between the substance collagen and the soluble matter extracted from certain vegetable materials and known as tannin. It is the mechanism of this reaction that is to be considered.

The fibrous structure of the collagen of hide makes any quantitative study of the chemical and physical properties of this substance extremely difficult. On the other hand, gelatin, which is derived from collagen and which is free from complications due to such structure, resembles collagen so closely in many of its properties that investigations dealing with purified gelatin have thrown considerable light upon the nature of collagen.

As a result of very extensive researches, the theory has been developed that any continuous mass of gelatin is not built up of individual molecules, but of chains of atoms forming a three-dimension network with interstices very much larger than the simpler molecules and ions, although still too small to be detected microscopically. Of the many pieces of evidence leading to this view,[1] the following may be given brief mention. The viscosity

* Presented at the Colloid Symposium of the 59th Meeting of the American Chemical Society at St. Louis, Mo., April 15, 1920.

[1] See also "The Structure of Gelatin Solutions" by F. C. Thompson, *J. Soc. Leather Trades' Chemists*, 3, 209 (1919).

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of a freshly prepared gelatin solution increases with time, is very much lowered by simply shaking or stirring, and slowly rises again upon standing. Although the viscosities of gelatin solutions are extremely high, they have vapor pressures nearly equal to that of water, crystalloids diffuse through them almost as rapidly as through water, and electrolytes dissolved in them show conductivities nearly as great as in water alone. Distortion of gelatin jelly in one direction produces double refraction. Not only are jellies elastic, but even gelatin solutions too dilute to set will resist a very small though continuously applied stress indefinitely, so long as the concentration of gelatin is greater than 0.18 per cent. If gelatin solutions of different concentrations are allowed to set and are then dried out to the same extent, they are not identical as is shown by the fact that, if immersed in water, the sample which was more dilute at the time of setting will swell to the greater extent by imbibition of water. The network structure just described is the only explanation yet offered that is entirely compatible with the above facts.

Enough work has been done upon collagen to show that it must have an internal structure similar to that of gelatin, and the same is true for other jellies, notably agar-agar. The enormous specific surface necessitated by such structure is probably what gives these jellies in so marked a degree the properties generally attributed to the colloid state.

A condition essential to vegetable tanning is that the liquor must be slightly acid. The function of this acid is more clearly illustrated by reference to the gelatin-hydrochloric acid equilibrium. As has often been shown, gelatin is amphoteric and resembles the simple amino-acids in its behavior towards acids and alkalies. When a plate of gelatin is immersed in a dilute solution of hydrochloric acid, some of the solution diffuses into the interstices of the gelatin network, where combination takes place between gelatin and acid, with the formation of a highly ionized chloride of gelatin. In other words, hydrogen ions are condensed upon, or combine with, the network, giving it a positive electrical charge, which is balanced by the corresponding chloride ions now held in the absorbed solution. For every hydrogen ion in the absorbed solution there will be a corresponding chlorine ion, but in addition there will be the chlorine ions from the gelatin

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salt, making a greater total concentration of chlorine than of hydrogen ions. In the outer solution the hydrogen and chlorine ions will be of equal concentration. But it has been proved thermodynamically[2] that at equilibrium the concentration of hydrogen ion multiplied by the concentration of chlorine ion must have the same value in both phases. Put algebraically, if we call the hydrogen-ion or chlorine-ion concentration of the outer solution x, and in the absorbed solution we let y equal the hydrogen-ion and $y + z$ the total chlorine-ion concentration, then $x^2 = y(y + z)$. Inspection of this equation shows that $2y + z$ is greater than $2x$, or that the total concentration of ions of the absorbed solution is greater than that of the external solution, which indicates a greater total diffusion pressure from the jelly towards the outer solution than from solution to jelly. These opposing pressures can be made equal only by the chlorine ions from the gelatin chloride diffusing into the outer solution until they have the same pressure in both phases, but since powerful electrochemical forces hold these ions in the vicinity of the network, the result is an outward pull upon the network, which is manifest in the swelling of the gelatin plate until the excess diffusion pressure is balanced by the cohesive forces of the network. This has been worked out mathematically in some detail and has been confirmed quantitatively by experiment.[3]

Now the unequal distribution of ions between the absorbed and outer solutions will result in a difference of potential between the two phases, as will be apparent from Donnan's well known work on membrane potentials,[4] which can be represented with our system of notation by

$$E = \frac{RT}{F} \log \frac{-z + \sqrt{4x^2 + z^2}}{2x}.$$

This formula can be extended to cover cases where any number of acids or salts are present in solution, but for the present purpose it will be sufficient to retain the simpler formula, calling x the total concentration of electrolyte in the outer solution, z

[2] *J. Am. Chem. Soc.*, 40, 886 (1918).

[3] This JOURNAL, 13, 177 (1918).

[4] See W. C. McC. Lewis, *A System of Physical Chemistry*, pp. 275-286 (Longmans, Green & Co., 1919).

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the concentration of gelatin ions, and y the concentration of electrolyte in the jelly other than the ions from the gelatin salt. It is evident from the formula that increasing z, but not x, will raise the potential difference, while increasing x, but not z, will lower it. This means that the addition of any electrolyte to the solution which will not increase the concentration of gelatin ions, will lower the potential difference. In place of the gelatin plate, we may now substitute collagen, or hide fiber.

Tannin particles are all negatively charged in aqueous solution. It therefore follows that in the layer of solution immediately in contact with the surface of any particle there must be an equivalent number of positive ions to balance the electrical charge. In view of the acid nature of tannin, it seems probable that these are hydrogen ions, but this has no bearing upon our theory. Other ions from the tan liquor may freely diffuse into or out from this surface film of solution, but, at equilibrium, because of the presence of the positive ions balanced only by the charge on the tannin particle, there will be a distribution of ions in the surface film of solution different from that in the bulk of solution and consequently a difference of potential between these two phases will be set up. This surface film is clearly analogous to the solution absorbed by the jelly in the case of collagen and the above equation for potential difference will also apply in the case of the tannin particles with proper change of sign, but z will now represent the concentration of positive ions associated with the charge on the particles and y the concentration of electrolyte in the surface film other than the positive ions associated with the electrical charge.

Now the surface film of solution surrounding the tannin particles and the solution absorbed by the collagen of the hide fibers, each having a potential difference against the tan liquor as a whole, but of opposite sign, will tend to merge, and when this occurs, the positively charged collagen and negatively charged tannin will neutralize each other by combination, forming leather.

The practical value of this theory lies less in its explanation of the basic action of tanning than in its suggestion as to how to control the rate of tanning, which is a determining factor in the quality of the final leather. Many tanners use extreme care to keep the rate of tanning as low as practicable by starting the hides

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off in nearly exhausted liquors and very slowly working the stock up through stronger liquors until tanned. Great care is exercised also in the matter of selection of materials since some materials, like quebracho and hemlock, are very much more astringent than others, such as sumac and gambier.

According to our theory, the rate of tanning depends, not upon the absolute values of the electrical charges on the hide substance and tannin particles, but upon the sum of the absolute values of the potential differences which we have described and which can be varied by altering the electrolyte content of the liquors, even though the values of the charges may remain constant.

In our equation, we have two independent variables, and, if the value of either one is varied while the other remains constant, the potential difference will be altered accordingly. Let us consider the variation of x, with z constant, in the case of the tannin particles. Adding common salt to the liquor would increase x, and I doubt that it would have much effect upon z. Increasing x clearly lowers the value of E; in fact, as x increases without limit, since z is constant, E approaches the limit log unity or zero.

However, this lowering of the rate of tanning by lowering E has a practical limit. In the case of emulsions of cylinder oil, Powis has shown that so long as the absolute value of E is greater than 0.03 volt the emulsion is stable, but when E falls below this value, the emulsion quickly breaks. A parallel to this is shown with some tan liquors, where the addition of salt causes an immediate precipitation of tannin. This furnishes an excellent theory for the salting out of soaps, or other colloids, since it necessitates no decrease in ionization of the soap. The quantitative nature of the equation should make investigations along these lines very interesting.

It is not so easy to suggest means of regulating z, but in a recent piece of research we hit upon a method that looks very promising. We had in the past attributed the great difference in astringency between quebracho and gambier to a difference in the electrical charge on the particles. This view was of course only speculative, since we have as yet no data on the values of these charges. But we have now found that, if the various tanning materials be placed in order of increasing value for the ratio *per cent. tannin/per cent. non-tannin,* we have at once the order

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for increasing degree of astringency. This suggested that differences in astringency might be due, not to differences in the charges on the tannin particles alone, but also to the non-tannin, which consists largely of the hydroxybenzenes and their corresponding acids. We showed first of all that gallic acid, which is a typical non-tannin, is removed from solution by hide powder, but is afterwards readily washed out of the powder. We believe this to be due to the hide combining with the gallic acid just as it does with tannin, but not nearly so completely, and that in the case of gallic acid the action is readily reversible. This led us to believe that simply by adding gallic acid to quebracho we could cause a lowering of the value of the collagen ion in the tanning process and consequently retard the tanning action. This was completely verified by experiment in which we found that adding gallic acid to quebracho so as to give it the same value for the ratio *per cent. tannin/per cent. non-tannin* as in the case of gambier reduced the astringency of the quebracho practically to that of gambier.

This discovery throws a new light upon the function of the non-tannins in vegetable tanning. In general, tanning causes a change in volume of the hide. If the surfaces of a hide suddenly become completely tanned while the interior is still raw, the tendency for the middle and outer layers to have different areas will cause a distortion of the hide, and the tanner will say that the liquor was too astringent. Call the rate of combination of hide and tannin c and the rate of penetration of tannin into the hide substance p. This distortion will evidently be greatest where c/p is a maximum. Or we might say that any increase or decrease in c/p will cause a corresponding increase or decrease in the apparent astringency of the tan liquor.

Let us compare gallic acid with pyrogallol tannin, which Fischer has shown to be pentadigalloyl glucose. Both are acids comparable in strength with acetic. Like other acids they form compounds with hide substance, but the tannin compound is very stable while the gallic-acid compound is readily hydrolyzed. Another vital difference is that the molecular weight of the tannin is very much the higher, in consequence of which the gallic acid diffuses into the hide substance at a very much greater rate than the tannin does.

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This comparison shows that adding gallic acid to a solution of tannin should cause an increase in p and a decrease in c, and therefore in a decrease in astringency. The much greater rate of diffusion of the gallic acid allows it to penetrate the hide substance faster and to come into contact with the collagen network long before the tannin. When the slowly moving tannin reaches a given point on the collagen network, it finds it already occupied by gallic acid and has no alternative but to move on or else wait until the gallic-acid compound hydrolyzes enabling it to take its place. Tannin that otherwise would have combined with the outer surface of the hide is thus enabled to pass on into the interior and while the rate of tanning at any one point is very much slower, it proceeds more nearly uniformly throughout the whole hide, distortions due to uneven tannage are much less, if at all, noticeable, and the total time required for complete tannage may be lessened very considerably.

Certain so-called synthetic tanning materials are now widely used as preliminary tanning agents for heavy vegetable leathers because they later cause an increase in the rate of penetration of the tannin and thus greatly hasten the tannage. It seems likely that their chief function is that which we have described for gallic acid.

LEATHER AND GLUE*

By F. C. Thompson.

Research work, both purely scientific and technical, has been very small in quantity during the year 1918, and it is not easy to point to many definite and important advances in either theory or practice. This is of course due to the very small number of men who have been able to carry on research of any kind. The shortage of workmen, high wages, and need for rapid production have had the effect of turning the attention of many manufacturers to labour-economy. This is seen in the adoption of quicker processes, *e. g.* in liming and tanning, and also in the growing desire to lessen the handling of goods by making the fullest possible use of machinery. The effect of the war can also be recognized in the eagerness with which chrome tanning is being taken up by many who, until recently, have never attempted it. Apparently, after a long period of comparative neglect in this country, some effort is now being made to produce those chromed goods hitherto imported on a very large scale. Chrome tanning is not easy or safe without chemical control;

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indeed many tanners would describe it as impossible. For instance, one cannot regard the different one-bath chrome liquors on the market as equally suitable for all classes of goods and very awkward surprises are in store for the manufacturer who simply replaces one such liquor by another, perhaps on grounds of cost, without having it analysed and tested. On the other hand vegetable tanning has long been carried on by those whose strictly scientific knowledge was very slight indeed. Probably the reason for the comparatively late adoption and slow progress of chrome tanning in this country lies here, a process such as vegetable tanning, which gives greater scope for simple common sense, being more congenial to Englishmen. Now, however, the usefulness of the chemist in the leather works is widely appreciated, and a striking feature of the war period, and especially of the last year or two, has been the engagement of chemists by firms who had previously relied for success solely on accumulated works' experience. The great factor in this change is no doubt what we have learned from Germany, but much is due to the fact that vegetable tanning is losing its ancient predominance in the world—not that there is any sign of its disappearance. Tanning is indeed becoming more and more a chemical industry, and chemists are not nowadays kept simply to the control of raw materials and established processes, but, with the more progressive firms at least, are given their due share in the modification of present day methods and the working out of new ones.

No very great insight is needed to realise the future importance of synthetic tanning materials. Neradol D, brought on to the market just before the war, and apparently doubtfully received, proved to be of such practical importance that several firms in England began its manufacture immediately after German supplies were cut off, and it is probable that at no very distant date the tanner will have as large a variety of synthetic tannins offered him as he ever had of vegetable materials. Further, although Knapp must be pronounced to have been unsuccessful, at least in a commercial sense, in producing iron-tanned leathers, there is no doubt a great field of possibilities in that direction as is indicated by the steady taking out of patents. Knapp could have known but little of the chemistry and physics of colloids, whereas it is now realised how much the success of a process depends on a true appreciation of colloidal conditions. Iron solutions, though similar to chrome solutions in many ways, are far from being exactly like them in a colloidal sense, and in tanning, where ammonia is a strong alkali, and acetic acid a strong acid, conditions must of necessity be very delicately adjusted. Formaldehyde tanning, at present little understood, shows another direction in which the chemist will be of great service to the tanner. Future (and past) work on the reactions of this substance with proteins will have to be very carefully studied by those who wish to develop the process.

Before entering upon a discussion of technical and scientific advances during the year under review, something should be said on the question of raw materials. The leather industry utilises a by-product as its

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principal material. Hides are always of secondary importance when compared with the carcase from which they are taken, and sheepskins are worth not only less than the mutton, but less than the wool. Consequently, if the best hides and skins are to be obtained, great care with regard to branding, insect pests, flaying, curing etc., must be taken by those whose chief interest is in food production and not in leather manufacture. Apparently there is in many places a growing interest and activity with regard to the care of hides and skins, of which the world supply is too small to allow of preventible losses. A great effort to eradicate the cattle tick is being made in the United States[1], which has so far met with pronounced success. The method adopted is to give the cattle an arsenical dip, a treatment repeated every two weeks. Previous to 1909 swabbing and spraying by hand were the methods used, but these were abandoned when dipping was found to be so much more effective. The success attained is shown by the figures for the infected areas. In July 1906 these areas totalled 728,565 sq. miles, and in December 1917 no more than 349,253 sq. miles. The work is still in progress, and vast numbers of cattle have already been saved. In India[2] the Agricultural Department is issuing bulletins and endeavouring by other means to convince cattle owners and others of the great losses they incur by heavy and careless branding, and by unskillful flaying. Branding may easily cause a loss of several shillings per hide, whilst bad flaying may reduce the value to less than half. The opinion is widely held[3] that strong action, even involving international co-operation, should be taken to minimise the preventible loss of hides and hide values, especially at such a time as the present when the number of cattle is very small. It has been estimated that there are 28,000,000 fewer cattle in the world than before the war.

It is now no longer possible to rely on more or less wild trees, etc., for the necessary supplies of vegetable tanning materials. Cultivation has long been practised on the Continent, and it is now being tried extensively within the Empire. A definite endeavor has been made for some years to create a large industry in South Africa by cultivating the wattle and subsequently exporting the bark. A few figures with regard to this may be of interest. Exports in 1908 amounted to 24,849 tons (value £134,562); 1910, 41,344 tons (£219,433); 1913, 65,052 tons (£309,329); 1915, 40,027 tons (£195,244); 1916, 50,866 tons (£254,864); 1917, 41,318 tons (£223,982); 73 per cent. of the exports in 1913 came to the United Kingdom, but three-fourths of this was re-exported, principally to Germany. Very great interest is at present being taken in this important industry. Lately the manufacture of a concentrated wattle extract has been taken up in Durban and Pietermaritzburg[4]. One process for the preparation of the extract is on the lines of sugar extraction from the

[1] This JOUR., **13**, 69, 1918.
[2] *Lea. Tr. Rev.*, **51**, 730, 1918.
[3] *Ibid.*, **51**, 197, 1918.
[4] *Ibid.*, **51**, 400, 1918.

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sugar cane and is applicable to the green, undried bark. In another process, also applicable to green bark, the finely chopped material is introduced mechanically into a large leaching vat and moved across it and against a flow of hot water by means of bronze paddles. The infusion leaves the vat near the point at which the bark enters. Evaporation is carried out in a Multiplex evaporator and vacuum pans, and the finished product is run into gunny bags where is soon sets hard. The wattle extract industry is only in its infancy, the first shipment having been made so recently as 1916, but it is capable of enormous development in view of the excellent qualities of the extract. The wattle industry is also arousing interest in Australia,[5] whilst in India, the cultivation of native tanning materials, *e.g.* "avaram," is also receiving attention.[6] Great difficulties have been experienced during the war, and more especially lately, in securing adequate supplies of tanning materials, and it was found necessary to appoint a Government Committee to deal with the problem and allocate supplies. No doubt the situation will be partly relieved as more and more shipping becomes available though there must be a considerable shortage for some time to come.

A further effect of the war will be the diversion of the tanning of Indian hides from Germany to this country and to India itself. A regrettable feature of the last few decades was the steady drop in such tanning in this country, and the corresponding steady rise in Germany. For a considerable period before the war, the exports from India amounted roughly to 11,000,000 hides, of which 3,000,00 were tanned, and 8,000,000 raw hides. Immediately before the war, the tanned hides came to England, and the raw hides went to the Continent, whilst at one time about 1870, all the hides came here.[7] The Leeds district alone used to tan about 3,000,000 kips per annum. All this has been attributed to German commercial methods, but was no doubt largely due to the energetic exploitation of chrome tanning in Germany at a time when English manufacturers were doubtful of its value. Meanwhile large tanneries are being opened in India to deal with the hides in the country of origin, where there are large available supplies of tanning materials, both vegetable and mineral. Action is being taken to improve the general standard of Indian tanning.[8] Another interesting commercial feature is the establishment of large tanneries in Ireland, at Cork and Drogheda,[9] where again hides will be tanned without being first shipped. It is also interesting to notice that difficulties in enemy countries have been much greater than here. In Germany prizes, amounting in each case to M.20,000, have been offered for (1) substitutes for cod oil and other fish oils used in currying, (2) for substitutes for chrome salts, and (3) for means of economising in the use of vegetable tanning materials.[10]

[5] *Lea. Tr. Rev.*, **51**, 97, 1918.
[6] *Ibid.*, **51**, 420, 1918.
[7] Sir H. Ledgard, *J. Roy. Soc. Arts*, **66**, 274, 1918; This Jour., **13**, 218.
[8] *Lea. Tr. Rev.*, **51**, 83, 1918.
[9] *Ibid.*, **51**, 146, 580, 1918.
[10] *Coll.*, **17**, 197, 1918.

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HIDE STRUCTURE AND PROCESSES PREPARATORY TO TANNING.

The anatomy and physiology of the various hides and skins used in leather manufacture is of great importance, and is very fully dealt with by A. Seymour-Jones in a long series of papers[11] which embody many independent views. For instance, the pelt, *i.e.* the skin from which epidermis and flesh have been removed, is not regarded as simply corium or "true-skin," as is sometimes the case, but as being more complicated in structure, and consisting of "grain-membrane," "fibre-bundle layer," *stratum adiposum,* and corium. The author therefore urges that it is entirely mistaken to regard the pelt used for tanning as being simply composed of fibre bundles, and considers that this view has led to much misunderstanding of wet-work processes. In the "grain" and "flesh" portions obtained on splitting hide or skin we have two things which are structurally entirely distinct. Indeed, instead of regarding the original skin as having two main parts, we must consider it to have three, namely epidermis, true-skin, and corium. These papers (which are excellently and liberally illustrated) cannot, however, be summarised here, though many points of great interest to tanners are discussed. W. Moeller[12] is in agreement with Seymour-Jones in insisting that pelt is not a single protein, and in emphasising the importance of elastin, which is never tanned, but becomes simply encased in tannin, and which does not yield gelatin on boiling. The principal action of bating, according to both authors, is not in the effect on collagen, but in the removal of elastin. Unless this is completely accomplished the necessary softness and "feel" of the finished leather cannot be attained. The presence of elastin is one of the main features of the true skin as distinct from the corium. In other papers Moeller[13] develops a theory of the ultimate structure of the hide and leather fibre, of which the main idea is that hide fibrils consist of chains of ultra-microscopic mixed crystals (micelles) of collagen and its products of hydrolysis. The collagen molecules unite to form crystals, probably polyhedric and elongated in shape, but which tend to a more spherical form on swelling when they become completely surrounded by the decomposition products. In gelatin the collagen micelles have almost all disappeared, and the products of hydrolysis have increased at their expense, forming a network. Tanning causes a twisting of the micelles, a phenomenon which can be observed microscopically. The theory is developed at length, but is not very easily followed, and appears to the writer to out-run the experimental evidence, though of course an ultimately crystalline structure of hide fibre is probable in view of von Weimarn's work on the colloidal state. The difference between the above theory and the views of Procter on the nature of gelatin jelly *i.e.* that it is a molecular network, is not very great; Moeller holds that there is the formation of ultramicroscopic crystals before the network is formed.

[11] *J. S. L. T. C.*, **1** and **2**, 1917 and 1918.

[12] *Coll.*, **17**, 105, 125, 1918; *J. S. L. T. C.*, **2**, 246, 1918.

[13] *Coll.*, **17**, 137, 157, 202, 230, 1918; *J. S. L. T. C.*, **3**, 1919; Abst. This JOUR., **14**, 124, 1919.

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It must however be borne in mind that the ultramiscroscope gives no proof of structure in gelatin jellies or solutions, and on the other hand that gelatin can be crystallised.

Liming.—In the practical liming of hides for unhairing there is very considerable advance to report. Acceleration of the process by means of sodium sulphide and other chemicals has been widely practised for many years. but despite the fact that suspension liming was patented by Conyers and Pullein[14] so long ago as 1874, no improvements in the mechanical part of liming have been generally adopted in England until very recently. Now, however, manufacturers are seeking to save time and labor, and rapid methods have come to stay; indeed ten days' liming for sole leather is spoken of as a thing of the past. In the Conyers and Pullein method, hides and skins were simply hung over rails within the pit, whilst spaces were left at the ends of the pit to allow of apparatus for agitation of the lime liquor. Other processes used the same principles. In the old German "Drehkälk" the hides were suspended from arms radiating from a central vertical rotating shaft. The pit was circular and the hides themselves acted as stirrers. Agitation has been secured in other cases by a kind of screw-propeller working underneath the suspended hides (which were protected by lattice-work), by blowing air into the pit (a method still in use), or by rocking the suspended hides. Heating the lime liquor has been suggested by Conyers and Pullein and many others, but seems to be totally unsuitable for sole leather hides, which, although rapidly unhaired, are badly plumped and very loose in the grain. Such processes have, however, failed until recently to meet with general adoption in this country, and the almost invariable method of liming has been simply to allow the goods to lie in the pits. A recently patented process which appears to be very successful is that of T Melbourne and B. H. Tilson.[15] Hides are slung in the limes by the neck and tail, the hair side being kept uppermost, whilst the liquor is agitated by an oscillating paddle working along the bottom of each pit. The saving in labor is very great, as the hides are never handled from their entering the limes until they are ready for unhairing; the time needed is at least halved, and a great saving in lime is effected. This last point is of considerable interest, for although water will dissolve only a very limited quantity of lime, it is found in practice that large quantities are needed. According to von Schdoeder, 6 grams. per litre is sufficient, but this amount, although four or five times as much as the water can dissolve, is much less than is used in practice. Ten pounds of lime per hide is a frequent allowance with ordinary liming methods, whereas with the usual pits, ½ lb. per hide would produce saturation. However, if an agitation method such as that just described be used, 3½ lb. of lime per hide is sufficient, though this is still a large excess, and shows how much lime is needed to maintain the full strength of the solution in

[14] Eng. Pat., 4,198, 1874.
[15] Eng. Pat., 117,581.

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contact with the hide. It is claimed by a writer[16] on the Melbourne-Tilson process that it has many incidental advantages, such as absence of lime stains, decreased loss of hide substance, and the ease with which liquors can be run away. However, any successful mechanical arrangement securing agitation of the liquor and involving suspension of the hides would be sufficiently effective.

Other Processes.—There have been no striking developments in deliming and bating during the year under review. H. R. Procter[17] has again called attention to the regeneration of organic acids used in deliming by the addition of regulated quantities of inorganic acids, such as sulphuric acid, to the solution of the calcium salt formed in the process. E. Luksch[18] has patented the use of the waste liquors from the manufacture or tartaric acid for deliming and bating.

Tanning.

The invention of synthetic tanning substances goes on apace, and it is of course impossible to say anything yet with regard to the technical value of the individual products. Some of these substances are of the familiar type obtained by condensing aromatic compounds and their sulphonic acids with formaldehyde.[19] For example, formaldehyde, *B*-naphthalenesulphonic acid, and naphthalene are allowed to interact in sulphuric acid of non-sulphonating strength. Several recent patents, however, describe the manufacture of tanning substances without the use of formaldehyde, which is quite a step in advance, especially as many of them are made from very cheap materials.[20] For instance, the product obtained by heating Caucasion "naphtha" with sulphuric acid is mixed with phenolsulphonic acid and heated. In another case[21] sulphonic groups are introduced into naphthol pitch or aromatic compounds of high molecular weight. It is evident that the possible sources of synthetic tanning materials are very numerous.

A. Turnbull and T. B. Carmichael[22] patent a very interesting tanning process involving the use of starch. Vegetable tanning extracts or basic chrome salts are dissolved in starch jelly, with which hides and skins are then treated, either in pits or drums. This process can be used for a great variety of leathers and allows strong solutions to be used safely in the first stages of tanning. The following example may be given to show the strength of liquors used: 500 lb. of chrome alum is dissolved in 125 gals. of hot water, and the solution is made basic by the slow addition of 64 lb. of soda ash previously dissolved in 250 gals. of hot

[16] *Lea. Tr. Rev.*, **51**, 738, 1918; Abst. This Jour., **14**, 76, 1919.

[17] *J. S. L. T. C.*, **2**, 121, 1918; *J. S. C. I.*, 343A, 1918.

[18] Ger. Pat., 305,898.

[19] U. S. Pat., 1,278,229.

[20] Ger. Pat., 303,640; Eng. Pat., 116,933; Eng. Pat., 116,936; Eng. Pat., 116,934.

[21] Ger. Pats., 304,859 and 305,777.

[22] Eng. Pat., 110,470.

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water. The liquor is heated to a temperature above 180° F., and 250 lb. of starch stirred in. The mixture on cooling is used directly for tanning. A quantity of vegetable extract, say 500 lb. at 125° Bark., may be added to the above before the starch. A writer in the Leather Trades Review points out that C. F. Cross similarly employed a strong tanning solution with a vegetable gum as the medium. The writer of this report has seen excellent samples of leather tanned by the starch process.

B. Levin[23] describes a pyrophosphate tannage in which the prepared hides are first treated with an alum solution and then with sodium pyrophosphate. The insoluble aluminium phosphate is thus produced within the hide and not in the tanning liquor, as in the case of an earlier process on similar lines, according to which the sodium pyrophosphate is added to the alum solution and the hides treated with the mixture. Precipitates will enter and in some sense tan hide on drumming. Procter long since showed that tanning could be accomplished with the "insolubles" of quebracho extract; this he regarded, however, as the effect of very slightly soluble substances having great affinity for hide.

Wood pulp extract is utilized by J. K. Tullis[24] in conjunction with ordinary tanning materials or with sodium bichromate. Patented processes using the ordinary materials are neither numerous nor very novel. L. A. Groth[25] has taken out a patent with regard to his well-known process of electro-tanning, whilst others have patented small modifications of established methods.

An interesting process is described by O. Röhm[26] for improving alum tannages. If the aluminium is used in the form of acetate or formate, or if formic or acetic acid is used with alum, the resulting leather is unusually resistant to water. Röhm[27] has also taken out patents for iron tanning. This he carries out by treating hides with an aldehyde before or at the same time as tanning with iron salts, *e. g.*, hide is treated with formaldehyde in weakly alkaline solution, and then with basic iron chloride. The leather is then neutralized in the same way as chrome leather, or treated with solutions containing precipitants of iron, such as ammonia, phenols, vegetable tannins, etc. This process may be combined with chrome or alum tanning.

There has been considerable interest taken in the sulphur dioxide chrome liquor, *i.e.* the basic liquor obtained by reducing bichromate with sulphur dioxide without the use of any acid. This liquor was referred to by H. R. Procter[28] in the Cobb lectures for 1918, and is now being very widely used, largely on account of the simplicity of its production and the way in which it can be used for many varieties of chrome leather. The

[23] Eng. Pat., 117,941.
[24] Eng. Pat., 117,922.
[25] Eng. Pat., 116,334.
[26] Eng. Pat., 110,750.
[27] Eng. Pats., 103,827 and 104,338.
[28] *J. R. S. A.*, **66**, 747, 776, 1918; This Jour., **13**, 582, 1918.

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writer of this report can testify to its remarkably quick tanning powers. The equation put forward by Procter to represent its formation is:

$$Na_2Cr_2O_7 + 3SO_2 + H_2O = Na_2SO_4 + 2Cr(OH)SO_4.$$

This corresponds to a basicity ratio Cr: SO_4 = 52: 96, a figure confirmed by analysis. Whether, however, the equation represents the true course of the reaction is rather open to question, as Bassett[29] some years ago showed that solutions could be obtained which contained complex ions and did not give the ordinary reactions. The Procter-McCandlish method of analysis involves boiling the solution, and heat is developed in the preparation of the liquor, causing boiling, if pure sulphur dioxide is rapidly led into a strong solution of bichromate. Bassett conducted his experiments with very dilute solutions, which would prevent any considerable rise of temperature. These considerations may be of importance in the preparation of the liquor.

The subject of tanning should not be left without some remarks on the mechanical side of the process. Here again rapidity is aimed at so far as is consistent with a proper quality of leather. Drum tanning for heavy leathers has not been regarded with favor in the past and it is generally recognized that the process is too drastic. It is, however, possible to tan rapidly with the aid of mechanical means and produce leather as good as the pit-tanned kind. This is done by keeping the hides in motion in the liquors by dragging them through or by a modified drumming arrangement whereby motion of the hides or liquors is secured, without the sudden bending and stretching, etc., to which leather is subjected in simple tumbling. Such methods are enjoying an increased vogue which has been a notable feature of the last year or two.

Analysis.

Many analytical papers published during 1918 are concerned with the analysis of leather itself, a problem which is certainly not yet completely solved. Early in the year a detailed scheme of analysis was agreed upon by the Government, which, although found to give very uniform results in different hands cannot be regarded as final.[30] For instance, C. D. Wilkinson[31] soon showed that two hour' drying in vacuo cannot give concordant results for moisture unless the pressure is exactly specified. The determination of water-soluble matter gives good agreement, but only, apparently, because the method is given in great detail, and not because all water-soluble matter is removed. The method is, essentially, percolation in a Procter extractor with 1 litre of water at 45° C. for three hours. The determination of nitrogen by Gunning's modification of Kjeldahl's method sometimes involves a very long digestion (though not often with sole leathers, for which the authorized scheme was specially intended) and this is a source of error according to Sörensen's recent work on egg-albumin. Very great importance attaches to the method of preparation of the sample for analysis *i.e.* whether it is ground or simply

[29] *J. Chem. Soc.*, **33**, 692, 1903.

[30] *J. S. L. T. C.*, **2**, 51, 1918; *J. S. C. I.*, 342A, 1918.

[31] *J. S. L. T. C.*, **2**, 132, 1918; *J. S. C. I.*, 343A, 1918.

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cut up. On this point F. P. Veitch and R. W. Frey[32] have made careful experiments, and not only confirm the usual belief that heating during grinding causes considerable and irregular losses in moisture, but also show that such heating causes similar losses in water-soluble matter. This was certainly not generally recognized before, but the explanation lies in the oxidation and anhydrization of uncombined tannin, which is thus rendered insoluble. It is possible, as Veitch and Frey showed, to construct a machine of circular saw-blades having specially formed teeth, which will not cause any material heating, but many analysts consider cutting by hand to be much the safest procedure. The Society of Leather Trades Chemists has recently appointed a committee to work on the whole field of leather analysis with a view to improvement and standardization of methods, and no doubt these points will be taken up.

J. A. Wilson and E. J. Kern[33] have recommended for fat extraction a mixture of equal parts of ethyl ether and carbon tetrachloride. Petroleum spirit, which is usually employed, has not sufficient solvent power, especially in the presence of oxidized fatty acids. Ethyl ether and carbon tetrachloride are each better in this respect, but have disadvantages when used alone. The boiling-point of the tetrachloride is too high for the extraction of leather, and something of the nature of burning is caused. The mixed solvent is free from this objection and is also less inflammable than petroleum spirit. Wilson and Kern also criticise Levi and Orthmann's method of extraction, according to which a definite volume of petroleum spirit is allowed to stand with the leather in a stoppered bottle for 24-72 hours. An aliquot portion of the solvent is then withdrawn and evaporated. In reply, L. A. Levi and A. C. Orthmann[34] state that the mixture of ethyl ether and carbon tetrachloride dissolves much that is neither fat nor oxidized fat from vegetable tanned leathers, and that it removed considerable quantities of dyestuffs and chrome soaps from chrome leather. They also defend their own method by new experimental results.

T. Mann[35] very fairly criticises the usual mode of stating the amount of sodium sulphate in leather, which is simply a calculation from the sulphates present in the ash, after deducting the equivalent of any magnesium present. Mann argues that a determination of sulphuric acid associated only with soda is impracticable, and gives a convenient method for determining soda itself, since all sodium salts, being soluble, are equally objectionable. The determination of free sulphuric acid in leather has been the subject of a large amount of work by a special committee of the American Leather Chemists' Association.[36] The principal result has been to show the general reliability of the simple Procter-Searle method

[32] This Jour., **13**, 232, 1918; *J. S. C. I.*, 555A, 1918.

[33] This Jour., **13**, 138, 1918; *J. S. C. I.*, 343A, 1918.

[34] This Jour., **13**, 313, 1918; *J. S. C. I.*, 555A, 1918.

[35] *J. S. L. T. C.*, **2**, 19, 1918; *J. S. C. I.*, 342A, 1918; Abst. This Jour., **13**, 167.

[36] This Jour., **13**, 319, 1918.

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of evaporating with N/10 sodium carbonate solution, igniting, and finally titrating the alkaline ash. Further work is proposed for the investigation of special points. O. Riethof and C. T. Gayley[37] point out the importance of distinguishing the "soluble" from the "insoluble" leather ash, *i.e.* the ash from the water-soluble and insoluble parts respectively of the leather. They show that the sum of these two is always greater than the ash of the original leather unless very great care is taken in this latter determination to wash out soluble salts (*e.g.* sulphates) from the charred leather before igniting.

Not very much that is new has appeared with regard to the analysis of tanning materials. Here again an American committee[38] has been at work. Sixteen chemists analyzed four samples, with disappointing results. The greatest difference between analyses of a powdered chestnut extract was 2.64 per cent. of tannin, but in the case of divi-divi, this difference was no less than 12.28 per cent. No doubt there is difficulty in getting uniform samples from a consignment of this material, but for one analyst to find 42.09 per cent. of tannin and another 54.37 per cent. is disconcerting, especially in view of a long series of results by two chemists published by J. M. Seltzer,[39] in which excellent concordance is shown. It has been usually held that despite the empirical nature of the methods of tannin analysis, very good agreement can be obtained by different workers. There are indeed undeniable theoretical objections to the indiscriminate use of the hide powder process under any or all circumstances. This is well brought out in a valuable paper by J. A. Wilson and E. J. Kern,[40] who deal with the absorption of non-tannins by hide powder. This substance when chromed by shaking with a chromic salt, basic or normal, combines not only with chromium but with acid, sulphuric or hydrochloric. Even after thorough washing with water there is still present ionisable collagen salt. On the basis of the work of Procter and his collaborators on gelatin-acid equilibria, the authors show that the presence of, say, sulphate ions in the hide powder will cause a lessened concentration of electrolytes in the absorbed part of any electrolyte solution, and a corresponding increase in the concentration of the external liquor. For example, after shaking chromed and washed hide powder with potassium sulphate solution, the external solution was found to have a greater concentration by 4.6 per cent. (in one case) than originally. Thus, if electrolytes are present in a tannin solution, the external liquid, after shaking with hide-powder, will become more concentrated than before with respect to electrolyte non-tannins, and too high a figure for non-tannins will thus be obtained. Such an error will vary in extent according to the ratio of hide powder to solution. With non-electrolytes, to which Procter's work has not been extended, a similar effect is due to some salting-out effect caused by the ions of the collagen sulphate,

[37] This Jour., **13**, 7, 1918.
[38] This Jour., **13**, 382, 1918.
[39] This Jour., **13**, 9, 1918.
[40] This Jour., **13**, 429, 1918.

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provided that the non-electrolyte does not combine with hide powder. Such considerations as the above should have great influence on future improvements in tannin analysis.

The analysis of chromium compounds etc., has received attention from several writers. J. R. Blockey[41] proposes to determine the basicity of liquors (i.e., the ratio of chromium to SO_4 combined with chromium) by determining the concentration of hydrogen ions in the liquor by means of the hydrogen electrode. This method can, however, be applied only to liquors of the same concentration and made up in the same way, and will be principally useful for dealing with works stock-liquors. A. Harvey[42] points out that if chrome liquors contain ammonium compounds, these must be determined by distillation with alkali. The amount found must be reckoned off the caustic soda used in titrating the boiling liquor for acid combined with chromium, according to the Procter-McCandlish method. C. Smith and F. Enna[43] give a rapid modification of this method. K. Schorlemmer[44] and R. Lauffmann[45] deal with the determination of chromium in presence of iron.

Lactic acid has been the subject of papers by F. C. Thompson and K. Suzuki[46] and by A. Harvey.[47] The latter author gives a useful method for the very necessary determination of iron in commercial acids. The process is based on the colour developed with potassium ferrocyanide, since thiocyanate appears to be useless in lactic acid solution. Thompson and Suzuki, by experiments with pure lactide, show that this substance is an efficient deliming agent. This is not the usual opinion in this country, and tanners have declined to pay for lactide in lactic acid. Further, the separate determination of lactide is not easy, as its concentration is not fixed in a given sample, but varies with the dilution, being highest in concentrated solutions. Time of standing after dilution and temperature also exercise influence. Obviously the amount of lactide present in such a dilute solution as the tanner uses can only by chance be that found by an analyst.

One or two papers have appeared, on the estimation of sulphides in lime liquors. H. G. Bennett[48] maintains that ammonia is necessary in the solution of zinc sulphate and ammonium chloride used for titrating the sulphide. By this means the precipitation of zinc hydroxide by the lime and the escape of hydrogen sulphide are both prevented. D. McCandlish and J. A. Wilson[49] in reply maintain that this is not the fact. In the case of a lime liquor containing an ordinary amount of sulphide there is no

[41] *J. S. L. T. C.*, **2**, 205, 1918; This JOUR., **13**, 573.
[42] *J. S. L. T. C.*, **2**, 125, 1918; Abst. This JOUR., **13**, 558.
[43] *J. S. L. T. C.*, **2**, 213, 1918; Abst. This JOUR., **13**, 556.
[44] *Coll.*, **17**, 145, 1918; *J. S. C. I.*, 445A, 1918; Abst. This JOUR., **13**, 610.
[45] *Coll.*, **17**, 223, 1918; *J. S. C. I.*, 775A, 1918.
[46] *J. S. L. T. C.*, **2**, 115, 1918; This JOUR., **13**, 334.
[47] *J. S. L. T. C.*, **2**, 37, 1918; Abst. This JOUR., **13**, 225.
[48] *J. S. L. T. C.*, **1**, 2, 1917; This JOUR., **12**, 626, 1917.
[49] This JOUR., **12**, 633, 1917.

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odour of hydrogen sulphide even in the absence of ammonia, whereas with a liquor containing as much as 0.5 per cent. of sodium sulphide there is a distinct evolution of gas in the presence of ammonia. H. Hayes[50] suggests modifying the titration by adding excess of the zinc solution to a comparatively large quantity of lime liquor and estimating the excess of zinc remaining. The titrations by the direct method are usually very small, as lime liquors often contain no more than 0.1 per cent. of sulphide. In the opinion of the writer there is no need to trouble about great exactitude. An error of 10 per cent. in a liquor of 0.1 per cent. strength would mean nothing to a tanner.

Theory of Tanning, Etc.

Vegetable and Chrome Tanning.—J. A. Wilson[51] replies to Bennett's paper on the theory of tanning,[52] and while admitting the importance of the lyotrope series to which Bennett ascribes such great influence, declares its use in explaining tanning to be unjustifiable, since it is not understood and is unnecessary. Bennett's free use of the term "adsorption" is criticised on account of the vagueness of its meaning, and the view is maintained that many so-called cases of adsorption are instances of chemical combination. The strongest part, however, of Wilson's argument is his development on purely theoretical grounds of equations governing the behaviour of an elastic jelly when immersed in a solution of an electrolyte with which it combines chemically. The equations do not involve any ideas of lyotrope influence or adsorption, but are based on the orthodox conceptions of ionization and osmotic pressure, and further, they correspond quantitatively with the experimental findings in the case of gelatin and hydrochloric acid. Wilson maintains against Bennett the chemical theory of chrome tanning, on account of the positive charge borne by the particles of a chromic hydroxide sol; as gelatin is also positively charged under similar circumstances, there can be no electrical neutralization. The writer of this report considers that there is more to be said on this point, as it has never been decisively proved that chromic hydroxide is the tanning agent rather than basic salts. There are strong grounds for believing in the existence of definite basic sulphates, and it has been stated by Stiasny (though the writer cannot find the experimental evidence) that they are negatively charged colloids. The tanning action of a true hydrosol of ferric hydroxide is completely prevented by a protective colloid, such as egg-albumin, whilst the effect of a basic chrome solution is only slightly hindered. At the same time a fact must be mentioned which appears to tell strongly against an electrical neutralization theory—*viz.* that chromed gelatin absorbs as much tannin as ordinary material.

[50] *J. S. L. T. C.*, **2**, 258, 1918.
[51] This Jour., **13**, 177, 1918.
[52] *Annual Reports*, **2**, 370, 1917; This Jour., **13**, 91, 1918.

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Aldehyde and Quinone Tanning.—W. Moeller[53] vigorously supports a colloidal theory of formaldehyde tanning in opposition to Fahrion. He points out that formaldehyde readily polymerises, especially in presence of alkali (under which condition formaldehyde tanning is carried out) and considers that colloidal polymers are responsible for the tanning effect. Aldehydes which do not polymerise do not tan. Perhaps it is better to say that formaldehyde is the only one with any considerable effect. Further, Moeller questions the reality of the chemical combination of formaldehyde with proteins, though admitting the reaction with products of hydrolysis. W. Fahrion[54] replies that the necessary condition for tanning properties in an aldehyde is the presence of a methylene group united with an oxygen atom, a condition fulfilled by formaldehyde. He also urges that just as this substance reacts with amino-acids, so it can react with the free amino groups which Moeller admits to be present in proteins. Formaldehyde will also tan in alcoholic solution, which disproves the necessity of methyleneglycol, a body which Moeller claims to be the peptiser, formed by the action of water. The whole question is in need of further experimental work, and it should be recognized that a colloidal theory of aldehyde tanning does not stand or fall with Moeller's theory of peptization. There appear to be, however, strong grounds for regarding the process as simply chemical.

On the question of quinone tannage, Moeller and Fahrion are again in conflict, the former[55] upholding a colloidal and the latter[56] a chemical theory. Moeller states that the quinones which tan are unstable in aqueous solution and tend to form colloidal solutions. A stable quinone, such as anthraquinone which does not form colloidal complexes, does not tan. Moeller regards quinone tannage as an oxidation of free amino-acids present in hide, with the formation of quinol and quinhydrone; the oxidation proceeds to the formation of colloidal humins which are the essential tanning agents. Fahrion regards the process as simply a chemical combination which will take place on rubbing together dry quinone and hide-powder. If the product is extracted with alcohol and dried, it is found to be very resistant to water, and is therefore leather. The instability of quinone in aqueous solution is consequently irrelevant, and Moeller's peptisation theory is dismissed as superfluous.

Swelling Etc., of Gelatin.—H. G. Bennett[57] develops a new theory of the swelling of gelatin on very different lines from that of Procter. The contractile force of surface tension causes any liquid surface to be a zone of compression, and any increase in surface causes a corresponding extension of such zones. In a gelatin sol. an enormous surface is developed by the particles of the disperse phase, and consequently the com-

[53] *Coll.*, **17**, 25, 61, 1918; *J. S. L. T. C.*, **2**, 188, 1918; Abst. This Jour., **13**, 503 and 505.

[54] *Coll.*, **17**, 213, 1918; *J. S. C. I.*, 776A, 1918; Abst. This Jour., **14**, 83.

[55] *Coll.*, **17**, 71, 93, 210, 241, 1918; Abst. This Jour., **13**, 506 and 608.

[56] Loc. cit.

[57] *J. S. L. T. C.*, **2**, 40, 1918; This Jour., **13**, 270.

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pressed water is a considerable proportion of the total amount present. With increasing concentration there is gradual approach and ultimate contact of compression zones with a corresponding increase in viscosity, finally resulting in rigidity. Rise in temperature increases the kinetic energy of the particles and reduces the compression with consequent loss of viscosity. The structure of a jelly is therefore a continuous network of water under great compression. A jelly, even when immersed in water, has a surface tension which tends to resist swelling, and depends on the extent of the compression in the water of the jelly. As the jelly swells, therefore, the power of resisting swelling diminishes. Dissolved substances have an effect on the compressibility and other physical properties of water called the lyotrope effect, and strongly influence the compression of water in a jelly. Substances with a small or great lyotrope effect have a corresponding effect on the properties of gelatin jelly. Some dissolved substances in concentrated solution produce a stronger effect of compression than exists in the original jelly; the surface tension effect is therefore reversed and the jelly contracts and hardens. The repulsion of similarly charged particles is held to be the cause of swelling. This force diminishes rapidly with increasing volume until it is less than the more slowly diminishing contractile force. On the above grounds, assuming the electrical charges to be due to adsorbed ions, Bennett gives an equation for the force producing swelling, and deduces from it curves which correspond in type to those experimentally obtained. H. R. Procter,[58] in reply, objects to the term "lyotrope influence," as not conveying any definite meaning, and emphasizes the purely qualitative nature of Bennett's reasoning, whilst pointing out that his theory of acid swelling, accounts quantitatively for the observed facts. Procter's most serious objection to Bennett's theory concerns the statement that the surface of a liquid is in compression on account of surface tension. This he regards as mechanically impossible, as pressure momentarily set up in the surface layer would be immediately transmitted to the interior mass of liquid. The surface is actually a region of tension and lessened density. In any case compression does not cause large increases in viscosity. Further, colloid particles, though charged, are surrounded by an oppositely charged layer of ions, giving an electrically neutral complex. Thus no electrostatic repulsion can take place. Charged particles move in electrophoresis because the layer is continuously displaced in an opposite direction to that of the particle. A simple account of Procter's theory of swelling is given in the Cobb Lectures on "Recent Developments in Leather Chemistry."[59]

V. Kubelka[60] has recently published work on the absorption of acid by hide powder. In the case of pure hydrochloric acid the amount taken up is independent of the concentration of the acid solution. For instance, from acid varying in strength from N/100 to N/1, 1 grm. of dry hide

[58] *J. S. L. T. C.*, **2**, 73, 1918; This JOUR., **13**, 285.

[59] *J. R. S. A.*, **66**, 747, 776, 1918; This JOUR., **13**, 582.

[60] *Kolloid, zeits*, **23**, 57, 1918; *J. S. C. I.*, 665A, 1918; Abst. This JOUR., **14**, 24.

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powder fixes 0.738 millimols of hydrogen chloride. In the presence of sodium chloride the phenomena are more complex, and the absorption curve consists of two branches, the first reaching a maximum corresponding with the absorption of 1 grm.-mol. of hydrogen chloride by 977 grms. of hide powder. The author regards this as indicating the formation of a definite compound, and considers 977 to be the molecular weight of collagen. The second branch of the curve is of the normal adsorption type, showing that the compound first formed simply adsorbs further quantities of acid. The conclusion that a definite compound is formed is the natural complement of Procter's discovery in the case of gelatin and acid.

A large amount of work on gelatin, fibrin, etc., from the biological standpoint has been published in America. M. H. Fischer[61] and others have worked on the swelling of gelatin and fibrin in solutions of polybasic acids and their salts, and find that with gelatin in phosphate solutions minimum swelling occurs in a solution having the composition of practically pure monosodium phosphate. In citrate solutions the minimum swelling takes place in a solution of 40 per cent. of monosodium and 60 per cent. of disodium citrate. Fibrin has minimum swelling in rather different solutions. The work is vitiated by neglect to analyze the external solutions after the attainment of equilibrium. There are alterations in the composition of any solution in which a protein swells, and these have been ignored by the authors. A similar error is made by R. C. Tolman and A. E. Stearn,[62] who have studied the swelling of fibrin of acids. They assume that the acid absorbed is of the same concentration as the external liquid, which is quite contrary to the facts. It is interesting to note that these authors, like Bennett, attribute swelling to electrostatic repulsion of charged particles. W. O. Fenn[63] has worked on the effects of electrolytes on gelatin. He finds, for instance, that the amount of alcohol required to precipitate gelatin increases with increasing concentrations of salts in solution. Very small amounts of alkalis and acids entirely prevent the alcohol precipitation, whilst with larger amounts, the quantity of alcohol required diminishes slowly with increasing concentration of electrolyte. This hindering action of akalies and acids in small quantities is diminished by univalent salts such as sodum chloride. Divalent cations such as calcium are antagonistic to alkalis, but not to acids; the reverse is the case with divalent anions. J. Loeb[64] has also published several papers on gelatin. He finds that this substance after soaking in sodium chloride solution will swell much more in water or a weaker salt solution. This has, however, long been known through Procter's work, and Procter's view of swelling as due to the formation of ionisable gelatin compounds is put forward as the explanation. Loeb

[61] *J. A. C. S.*, **40**, 272, 292, 303, 1918; Abst. This JOUR., **13**, 128.

[62] *J. A. C. S.*, **40**, 264, 1918; Abst. This JOUR., **13**, 131.

[63] *J. Biol. Chem.*, **33**, 279, 439, 1918; **34**, 415; Abst. This JOUR., **14**, 299.

[64] *J. Biol. Chem.*, **33**, 531, 1918; **34**, 77, 395, 489; **35**, 497; Abst. This JOUR., **14**, 78, 214 and 216.

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also finds that a divalent cation such as calcium causes contraction, and this he regards as due to the formation of a non-ionisable compound. The limiting concentrations of neutral salts which just inhibit the additional swelling of gelatin depend on the valency and not on the nature of the ions. Experiments on the influence of electrolytes on other properties of gelatin, such as osmotic pressure, viscosity, and precipitation by alcohol, show a distint parallelism with the results on swelling.

Chrome Liquors.—Some interesting papers on the nature of basic chrome liquors have appeared. A. W. Thomas and M. E. Baldwin[65] have studied the acidity of these liquors by means of the hydrogen electrode and have obtained instructive results. The writer however sees no force in the authors' strictures on the basicity figure. This represents the ratio of chromium to sulphuric acid combined with chromium, and is variously expressed, in this country usually as 52: x. For instance, $Cr_2(SO_4)_3$ has the ratio 52: 144, and $Cr(OH)SO_4$ the ratio 52:96. Such a figure, obtained by analysis, gives the empirical composition of the chromium compounds in the liquor, and is valuable information from the tanner's point of view, as variations in basicity mean very real differences in the tanning effect. The acidity of a liquor is due to hydrolysis, *e.g.*—

$$Cr_2(SO_4)_3 + 2H_2O \rightleftharpoons 2Cr(OH)SO_4 + H_2SO_4$$

The extent of this hydrolysis varies with dilution and temperature, but it in no way corresponds with the basicity of the chrome compound. Thomas and Baldwin, however, criticise the basicity figure because it bears no relation to the acidity as found by the hydrogen electrode, whereas, in this country at least, no one supposes that basicity figures reveal anything else than the empirical composition of the liquor. The authors found that moderate dilution of a basic liquor caused an immediate drop in hydrion concentrations and a further slow decrease in the course of several days. Very great dilution, however, caused an immediate drop to a final value. The decrease in hydrion concentration in this case does not correspond exactly with the dilution, but represents a greater degree of hydrolysis. A stock liquor, for instance, with $(H^{\cdot}) = 0.0049$, was diluted to twenty times its volume, when (H.) fell immediately to 0.0008, and after seven days further diminished to 0.00055, thus showing a final degree of hydrolysis rather more than twice the original. However the interpretation of this last result is complicated by the settling out of a precipitate. A concentrated chromic sulphate solution behaved rather differently, the immediate drop in hydrion concentration corresponding roughly to the dilution, after which ensued a slow increase to a final equilibrium value. A very valuable feature of the paper is the experimental proof afforded that the hydrolysis of chromium compounds at ordinary temperatures is a very slow process. J. R. Blockey[66] also publishes work on chrome liquors and verifies the greater hydrolysis of green as compared with violet chromium solutions. The hydrion concentration in the former is over ten times that in the latter. It is a well-

[65] This Jour., **13**, 193, 1918.

[66] *J. S. L. T. C.*, **2**, 205, 1918; This Jour., **13**, 573.

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known fact that green solutions swell pelt much more than violet ones, and generally behave (in the inversion of cane sugar for instance) as being more acid. Green solutions are produced by boiling, and according to Blockey the color is probably due to chromium ions, whilst the unionized compound is violet.

Another paper by Thomas and Baldwin[67] deals with the role of neutral salts in chrome liquors. The effect, as yet unexplained, of sodium and ammonium chlorides is to increase the hydrion concentration very considerably. This is even the case when salt is added to dilute sulphuric acid. Sodium and ammonium sulphates retard the formation of a precipitate on dilution, and the effect increases with the amount used, but there does not appear to be any definite hydrion concentration at which precipitation begins.

Chemistry of Vegetable Tannins.—Nothing has recently appeared of such great interest as E. Fischer's investigation of gallotannic acid referred to in the report for 1916. The same chemist has, however, continued work on tannins and tannin derivatives, and has recently carried out a new synthesis of digallic acid.[68] 3.5-Diacetylgallic acid is condensed with triacetylgalloyl chloride, yielding penta-acetyl-*p*-digallic acid. Curiously enough, when this compound is hydrolysed with cold dilute ammonia *m*-digallic acid is formed. Another paper by Fischer[69] on chebulic acid shows that although this substance yields gallic acid and dextrose on hydrolysis, it is not related in structure to the galloyl-glucoses.

Glue.

There is little to report under this head. A. W. Clark and L. DuBois[70] have published a paper on the "jelly value" of glues and gelatins, in which they give details for determining the weakest solution which gives a solid jelly at 10° C. If a 6 per cent. solution of a sample is solid at this temperature whilst a 5 per cent. is liquid, the material is said to have a comparative jelly strength of 6 per cent. C. F. Sammet[71] measures jelly strength by determining the ease with which swollen particles of glue melt and slide when placed on an inclined brass plate, one end of which is dipped in water at 40° C. The poorer grades melt and slide down the plate more rapidly than the better glues. A method for directly determining the adhesiveness of glue has been worked out by M. Rudeloff.[72] The sample should be dissolved in 150 per cent. of water, and the solution applied to wooden surfaces carefully prepared and of prescribed area. The wood should have been previously heated in dry air at 40° C., and after the glued surfaces are brought into contact, the film is left to dry under a pressure of not less than 0.84 kilo. per sq. cm. The force required to pull apart the two pieces of wood is then measured by a suitable machine.

[67] This Jour., **13**, 248, 1918.

[68] *Ber.*, **51**, 45, 1918.

[69] *Ber.*, **51**, 298, 1918; Abst. This Jour., **14**, 79, 1919.

[70] *J. I. E. C.*, **10**, 707, 1918.

[71] *J. I. E. C.*, **10**, 595, 1918.

[72] *Mitt. K. Materialprüf*, **36**, 2, 1918; *J. S. C. I.*, 743A, 1918.

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CONTENTS

The Forest Products Laboratory Decennial Celebration - - 399
The Sixth National Exposition of Chemical Industries - - 400
The Seventeenth Annual Meeting - - - - - 401
The Determination of Inorganic Impurities in Sulphated Oils. By Ralph Hart - - - - - - - 404
Epsom Salts in Leather—1920 Committee Report. By R. W. Frey, Chairman - - - - - - - 406
Determination of Glucose in Leather—1920 Committee Report. By J. S. Rogers, Chairman - - - - - - - 411
Abstracts - - - - - - - - 433
Patents - - - - - - - - 447

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W. K. ALSOP . . . . . Editor and Manager
G. W. SCHULTZ . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

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The American Leather Chemists Association

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THE FOREST PRODUCTS LABORATORY DECENNIAL CELEBRATION.

The Forest Products Laboratory was organized by the U. S. Forest Service in 1909 and formally opened in June, 1910. It is conducted in co-operation with the University of Wisconsin. During the ten years of its existence the efforts of the laboratory have been devoted to the development of improved methods and processes for the better utilization of forest products of all kinds, and to the direct assistance of the industries concerned.

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A good many men acquainted with the work of the laboratory have expressed the thought that the laboratory and the service rendered by it should receive some mark of recognition or appreciation from the industries which it serves. In response to this thought, the decennial celebration has been planned, and the General Committee organized to carry out the detailed arrangements. The present plans call for a two-day program, including addresses by men prominent in science, industry and commerce; inspection of the laboratory; a banquet; and various other forms of instruction and entertainment.

A cordial invitation to attend is extended to the Association and all who are interested.

THE SIXTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES.

The 1920 annual, which is the Sixth National Exposition of Chemical Industries returns to the Grand Central Palace in New York where it will be given during the week September 20th to 25th inclusive. The Exposition this year will be more pretentious than ever, it will be the largest distinctly industrial Exposition ever held, and will surpass its own predecessors by one-third.

This year the Exposition will have three special sections, the Electric Furnace Section, the Fuel Economy Section, and the Materials Handling Section; the two latter are new sections. The first will as its name implies be one of electric furnace exhibits; the Fuel Economy Section will consist of exhibits of machinery and apparatus, furnaces, producers, stokers and all devices for the economic utilization or more efficient combustion of fuel. The possible exhaustion of our fuel reserves in the not far distant future and the present high cost of fuel makes this section one of much interest to all industrial plants. The Materials Handling Section will be a series of exhibits of machinery and equipment for the handling of material such as: conveying, transporting, elevating, included in this will be weighing, measuring and power transmission equipment. So important have these mechanical features become for all industrial plants due to the shortage and high-wage for man-power that an unusual interest is expected in this new Section.

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THE SEVENTEENTH ANNUAL MEETING.

The seventeenth annual meeting of the A. L. C. A. held at Atlantic City, May 27, 28 and 29th proved to be very successful. The attendance was good and the interest and enthusiasm displayed by the numerous questions and discussions was encouraging. The meeting was opened Thursday morning with the address of welcome by President R. W. Griffith which has already appeared in the June number of the JOURNAL. The report of the Secretary-Treasurer, H. C. Reed, followed. The Secretary's report consisted of a statement of the membership, a summary of which is as follows:

Total number of active members May 1, 1920	152
Total number of associate members May 1, 1920	211
Total number of mutual members May 1, 1920	45
Total membership	408

This total shows an actual loss in membership of 13 during the past year.

The Treasurer's report for the past year was as follows:

GENERAL ACCOUNT.

Receipts.		
Cash on hand May 1, 1919		$2,520 77
Dues	$2,401.43	
Interest, and uncashed checks and credit	118.39	2,519.82
		$5,040.59
Disbursements.		
Annual meeting expenses	$ 277.22	
Council meeting expenses	155.92	
Secretary's expenses	495.84	
Printing, postage, expressage, supplies	132.64	
Printing Convention Programs	190.87	
Dues paid Society Leather Trades Chemists	10.00	
Printing Official Method Booklets	68.19	
To checks uncashed prior to May 1, 1919	42.50	
To foreign exchange and checks not honored	43.73	
From JOURNAL Account	1,879.20	$3,296.11
Balance on hand in bank, May 1, 1920		$1,744.48

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JOURNAL ACCOUNT.

Receipts.

From advertisers	$1,585.74	
From back numbers	219.90	
From bound volumes and Ten Year Index	771.95	
From subscriptions	424.60	$3,002.19
Disbursements.		
JOURNALS	$2,929.75	
Reprints	716.95	
Abstracts and translations	79.00	
Ten Year Index	489.38	
Bound volumes	120.47	
Editor's expenses	451.99	
For back numbers of JOURNAL	69.85	
Insurance on JOURNALS	19.00	
Subscriptions to JOURNALS	5.00	$4,881.39
To General Account		$1,879.20
(Deficit)		

SUMMARY.

Cash on hand May 1, 1920		$2,520.77
Receipts, General Account	$2,519.82	
Receipts, JOURNAL Account	3,002.19	5,522.01
		$8,042.78
Disbursements, General Account	$1,416.91	
Disbursements, JOURNAL Account	4,881.39	6,298.30
Balance in bank May 1, 1920		$1,744.48
Liberty Bond, second issue, 4 per cent		1,000.00
Interest, not drawn		40.00
Total		$2,784.48

Since May 1, 1920, checks amounting to about $500.00 have been received.

These reports were followed by a committee report by G. W. Schultz on the Analysis of Sulphonated Oils which was published in the May JOURNAL (**15**, 283, 1920). J. A. Wilson read a paper on The True Tanning Value of Vegetable Tanning Materials by J. A. Wilson and E. J. Kern (This JOUR., **15**, 295, 1920), which provoked much interest and a lengthy discussion.

The afternoon session opened with a paper by A. A. Claflin on the Direct Measurement of the Plumping Powers of Tan Liquors. This address was an elaboration of the author's paper that appeared in the April JOURNAL (**15**, 234, 1920) with some additional experiments. G. L. Terrasse read a paper on the composition of hide substance which was followed by a description of a new

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method for the determination of sulphuric acid in leather by Dr. A. W. Thomas. The Effect of Humidity on the Strength and Stretch of Leather by F. P. Veitch and M. A. Hunt was then given. The Thursday session closed with a plea from Dr. Louis J. Matos to the leather chemist for an attempt to standardize the testing of dyes for the leather industry so that uniform results could be obtained.

The Friday morning session was devoted entirely to committee reports. The three committees on the sampling and preparation of leather for analysis reported progress. F. P. Veitch read the report of the committee on the determination of the moisture content of leather and J. F. Anthes read that on the determination of water solubles. J. M. Seltzer read the final report of the committee on the determination of total, soluble and insoluble ash in leather which has appeared in the May JOURNAL (**15**, 270).

The afternoon session was opened with an outline of the paper on the Retardation of Chrome Tanning by Neutral Salts by J. A. Wilson and E. A. Gallun. This paper has also been published in the May JOURNAL (**15**, 273). A. W. Thomas and M. W. Kelly presented a paper on the Time Factor in the Absorption of the Constituents of Chromic Sulphate Solutions by Hide Powder and this was followed by The Titration of Chrome Liquors by the Conductance Method by A. W. Thomas and S. B. Foster. Then followed an interesting paper on the Unhairing of Hides and Skins by Enzyme Action by Dr. C. S. Hollander. The commercial application of the work of the Forest Products Laboratory was outlined by C. P. Winslow. This session was closed after a very interesting address by Dr. Buckner Speed entitled Invention, Research, Engineering, Manufacture.

Saturday morning reports were given by R. W. Frey, F. P. Veitch and J. S. Rogers, respectively chairmen of the committees on the Determination of Epsom Salts in Leather, The Determination of Oils and Fats in Leather and The Determination of the Sugar Content of Leather.

The meeting was then terminated with an executive session and the election of officers.

The vote on the two proposed changes in the by-laws of the Association, Section 8 [see this JOUR., **14**, 427 (1919)], and Section 7(a) [this JOUR., **15**, 130 (1920)], rejected them. On the

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first proposal 51 votes were cast and therefore 34 affirmative votes were necessary for its adoption. 28 voted yes and 23 voted no. The second proposal was defeated by a vote of 26 for and 41 against.

The officers elected for the ensuing two years were as follows: President, F. H. Small; Vice-President, J. A. Wilson; Secretary-Treasurer, H. C. Reed; ordinary Members of Council, J. S. Rogers and Roy H. Wisdom.

All papers delivered at this meeting which have not already appeared will be published in this JOURNAL as soon as possible together with discussions that occurred.

THE DETERMINATION OF INORGANIC IMPURITIES IN SULPHATED OILS.

By Ralph Hart.

Received June 16, 1920.

In the rapid method for the analysis of sulphated oils, proposed by the writer in 1917,[1] no provision was made for the determination of SO_3 bound as salt. By this method, organically combined SO_3 and alkali bound as soap are determined by titrations. In this paper, it will be shown that with this data and the additional determination of the ash, the SO_3 bound as salt and the other non-volatile impurities in such oils may be readily calculated, thereby avoiding an unpopular gravimetric analysis.

The ash of a sulphated oil may consist of the following compounds: Na_2SO_4, Na_2CO_3, and non-volatile impurities such as NaCl, Fe_2O_3, etc. The sulphate in the ash is partly due to the salt present in the original oil and partly to the combined SO_3, while the carbonate is the result of igniting the soda soap. Not all of the combined SO_3, however, will always be found in the ash, the exact amount depending on the fixed alkali bound as soap.

By incinerating the sulphated group, the following changes take place: $2RSO_4Na \rightarrow Na_2SO_4 + SO_3 + CO_2 +$ etc. It is evident, therefore, that unless fixed alkali as soap be present, half of the combined SO_3 will be volatilized. Furthermore, if the sulphated group has been only partially neutralized or neutralized with ammonia, the loss of SO_3 will be still greater. However, the determinations of the alkali bound as soap and of the combined SO_3 offer sufficient data from which to calculate the amount

[1] This JOUR., 12, 189 (1917); 14, 90 (1919); 15, 283 (1920).

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of the non-volatilized sulphate as well as the carbonate present in the ash, and by difference from the latter, the salts and other impurities in the oil may readily be found.

To determine the per cent. Na_2SO_4 in the ash due to combined SO_3, the following formula is applicable, where A_s represents the combined SO_3 expressed in mgms. KOH and A represents the alkali minus ammonia similarly expressed: Na_2SO_4 (due to combined SO_3) =

$$\frac{1}{10}\left[\frac{A_s}{2}+A\right]\frac{Na_2SO_4}{2.KOH}=\frac{142}{1120}\left[\frac{A_s}{2}+A\right]=0.0634\ (A_s+2A).$$

In using this formula, several precautions must be observed: (1) A represents only the alkali minus ammonia, which may be negative in the case of the presence of ammonium salts. The sign, however, is automatically taken care of by the formula[2] used in calculating the alkalinity. (2) This formula holds good only when $2A \lessgtr A_s$, when $2A > A_s$, substitute A_s for $2A$.

For determining the per cent. Na_2CO_3 in the ash due to excess fixed alkali as soap, the following formula should be used:

$$Na_2CO_3=\frac{1}{10}\left[A-\frac{A_s}{2}\right]\frac{Na_2CO_3}{2KOH}=\frac{106}{1120}\left[A-\frac{A_s}{2}\right]=0.0473\ (2A-A_s).$$

It is evident that when the term $(2A - A_s)$ is negative there can be no carbonate in the ash.

The per cent. of salts and impurities in the oil may now be calculated as follows:

Salt and Impurities =

$$\text{Ash} - 0.0634\ (A_s + 2A) - 0.0473\ (2A - A_s).$$

This formula was applied to a few analyses on sulphated oils reported by Dr. C. G. Bumcke,[3] with the following results:

	No. 3 Per cent.	No. 4 Per cent	No. 7 Per cent.	No. 10 Per cent.	No. 13 Per cent.
Combined SO_3 (C. G. B.).....	1.95	1.91	1.93	2.65	2.00
A_s (calculated) mgms. KOH.....	27.2	26.8	27.1	32.0	28.0
Na_2O as soap (C. G. B.).....	0.205	0.520	1.35	0.369	0.25
A (calculated) mgms. KOH.....	3.70	9.40	24.5	5.80	4.52
Na_2SO_4 due to SO_3 (calculated)...	2.19	2.89	3.43	2.76	2.34
Na_2CO_3 (calculated)	none	none	1.04	none	none
$Na_2SO_4 + Na_2CO_3$ (calculated)...	2.19	2.89	4.47	2.76	2.34
Ash (C. G. B.).....	3.05	4.46	5.14	6.01	2.51
Salts and impurities, new method..	0.86	1.57	0.67	3.25	0.17
Salts found (C. G. B.).....	0.74	1.51	0.71	2.79	0.16

[2] This Jour., 14, 266 (1919).

[3] This Jour., 14, 515 (1919).

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Comparing the last two rows, it will be observed that the calculated values for foreign salts are very close to those actually found by Bumcke, except for No. 10. This oil represented a fat liquor with considerable amount of salts in it and probably contained besides Na_2SO_4 also iron and aluminium oxides which would not be indicated by Bumcke's result, as he reports only the Na_2SO_4. The indirect method, however, includes all the foreign salts such as metallic oxides and NaCl which are entirely neglected by the present methods.

For the determination of total inorganic impurities by the new method, the following data is required: ash, combined SO_3 and alkali minus ammonia. In ashing, the sample should be thoroughly ignited to free it from carbon and to oxidize to the sulphate any Na_2S that might be formed by reduction—the addition of hydrogen peroxide may be necessary.

By the new method, foreign inorganic matter in sulphated oil is determined indirectly by calculation from data obtained for the other tests of the oil. The result indicates not only sodium sulphate but all other salts and non-volatile impurities.

New York, N. Y.

EPSOM SALTS IN LEATHER—1920 COMMITTEE REPORT.

By R. W. Frey, Chairman.

While the following preliminary results could not be obtained in time to be of aid in drawing up directions for collaborative work they are offered now for suggestions and for the guidance of next year's committee.

In assigning the work of this sub-committee the main committee on leather analysis made the following suggestions: ". . . determine whether or not it is best to ascertain the Epsom Salts in the ash or in the water solubles of the leather. Also work with special reference to the influence of the water of crystallization of Epsom Salts in the determination of moisture and water solubles in leather."

Comparison of Epsom Salts in the Ash and in the Water Solubles.—To gain some idea of the differences that might be obtained by these procedures magnesium was determined by the usual gravimetric method, in the total ash and in the ash of an

[1] Read at the annual meeting at Atlantic City, May 29, 1920.

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aliquot of the water solubles respectively, of four samples of commercial sole leather. The water solubles were obtained by the A. L. C. A. method of extraction. The results are given in Table I.

TABLE I.

L. & P No.	Preparation	Description	Per cent. $MgSO_4.7H_2O$ from Ash of leather	Per cent. $MgSO_4.7H_2O$ from Ash of H_2O ext.
34116	Sawed	Oak	3.43	3.16
34278	Planed	Union	5.58	5.38
34288	Planed	Union	5.47	5.31
34580	Sawed	Union	3.83	3.65

In all cases the Epsom Salts from the ash of the leather is slightly higher than from the ash of the water solubles, ranging from 0.16 per cent. to 0.27 per cent.

To show that all the Epsom Salts added as such to leather is recovered in the water extraction the following experiments were conducted. A stock solution containing 25 gms. of Epsom Salts per liter at 20° C. was made up from a sample of the following compositions.

COMPOSITION OF EPSOM SALTS USED.

Per cent.	Found	Theoretical
MgO	16.88	16.36
SO_3	32.44	32.48
H_2O by difference	50.68	51.16

Using this solution samples of three sole leathers were treated as follows:

A—5 gms. of leather only;

B—5 gms. of leather plus 10 cc. of the Epsom Salts solution or, calculating from the MgO determined in the stock solution, 5.16 per cent. $MgSO_4.7H_2O$ on the leather basis;

C—30 gms. of leather only;

D—30 gms. of leather plus 60 cc. of the Epsom Salts solution or 5.16 per cent. $MgSO_4.7H_2O$ on the leather basis.

After the samples with the added magnesium sulphate had become air dried, magnesium was determined in the ash of portions A and B and in the ash of aliquots of the water extracts of C and D. The results are incorporated in Table II.

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TABLE II.—Per cent. $MgSO_4.7H_2O$ Found.

L & P No.		34286	34566	36991
Leather Ash	A—leather only	2.35	2.39	0.31
	B—leather + 5.16% Epsom Salts	7.75	7.63	5.64
H_2O Ext. Ash	C—leather only	2.30	2.21	0.13
	D—leather + 5.16% Epsom Salts	7.50	7.52	5.51
	B-A	5.40	5.24	5.33
	D-C	5.20	5.31	5.38
	A-C	0.05	0.18	0.18
	B-D	0.25	0.11	0.13

The difference between the ash from portions A and B ranges from 5.24 per cent. to 5.40 per cent. and that from C and D varies from 5.20 per cent. to 5.38 per cent. showing that all the added Epsom Salts is recovered in the extraction. It will also be observed that here again on six determinations the magnesium sulphate from the ash is a little higher than from the extract, ranging from 0.05 per cent. to 0.25 per cent. This difference is probably due to insoluble or difficultly soluble magnesium compounds from the water and lime used in tanning.

The Influence of the Water of Crystallization of Epsom Salts in the Determination of Moisture and Water Solubles in Leather.—To determine the per cent. of the water of crystallization of Epsom Salts driven off in the drying of leathers for moisture, two samples of sole leathers containing practically no magnesium and glucose were selected. Three carefully weighed 5 gm. portions of each leather were treated as follows, using the stock solution of Epsom Salts previously referred to:

A—5 gms. of leather, plus 10 cc. of water only.

B—5 gms. of leather plus 8 cc. of the Epsom Salts solution—equivalent to 0.2 gms. of salt or 4 per cent on the leather basis.

C—5 gms. of leather plus 12 cc. of the Epsom Salts solution—equivalent to 0.3 gms. of salt or 6 per cent. on the leather basis.

After these samples had become air-dried they were transferred to weighing bottles and dried for 16 hours in the combined evaporator and dryer. The difference between the losses on drying of the treated and corresponding untreated samples will give the loss due to 0.2 gm. and 0.3 gm. respectively of Epsom Salts, from which the per cent. loss of the latter can be calculated. The results are given in Table III.

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TABLE III.

Five grams leather:	A		B		C	
	+10 cc. water		+0.2 grams Epsom salts		+0.3 grams Epsom salts	
Total charge:	5.0 grams		5.2 grams		5.3 grams	
L & P No.	34279	34292	34279	34292	34279	34292
Loss 16 hours drying.....	0.4360	0.4421	0.5163	0.5221	0.5557	0.5610
Treated—Untreated	——	——	0.0803	0.0800	0.1197	0.1189
Per cent. loss of Epsom Salts	——	——	40.1	40.0	39.9	39.6

Average loss in weight of Epsom Salts = 39.9 per cent.

To ascertain the parallel loss in drying for water solubles, water extraction was made in the regular way of the same two leathers used for Table III. Because of the difficulty of obtaining very closely agreeing extractions even with the same sample, it was deemed advisable to add the magnesium solution to aliquots of the same extract rather than to compare separate extractions of treated and untreated samples. Consequently three 500 cc. aliquots of each extract were made up as follows:

A—480 cc. leather extract plus 20 cc. water;

B—480 cc. leather extract plus 12 cc. Epsom Salt solution and 8 cc. of water—equivalent to 4 per cent. on leather basis;

C—480 cc. leather extract plus 18 cc. Epsom Salt solution and 2 cc. of water—equivalent to 6 per cent. on leather basis.

After thorough mixing, duplicate 100 cc, aliquots were dried for 16 hours in the combined evaporator and dryer. The difference between the weight of the residues from the leather extract blanks and from the extracts containing the magnesium sulphate will give the weight remaining from the drying of the latter from which the per cent. driven off can be readily found. The figures so obtained are included in Table IV.

TABLE IV.

Aliquot of leather extract containing:	A		B		C	
	0.0 grams Epsom Salts		0.06 grams Epsom Salts		0.09 grams Epsom Salts	
L & P No.	34279	34292	34279	34292	34279	34292
Weight of residue after 16 hours drying	0.1968	0.2582	0.2326	0.2947	0.2520	0.3133
Treated minus untreated..	——	——	0.0358	0.0365	0.0552	0.0551
Per cent. of the Epsom Salts left after drying	——	——	59.7	60.9	61.3	61.2
Per cent. loss of Epsom Salts	——	——	40.3	39.1	38.7	38.8

Average loss in weight of the Epsom Salts = 39.2 per cent.

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Before discussing the results it is desired to point out what would seem to be an unavoidable weakness in the procedure for the figures in Table III and IV. To keep the amount of added magnesium sulphate within a reasonable range of from 4 per cent. to 6 per cent. it was necessary to work with very small quantities of the salt and it will be readily realized that operating with materials such as leather and leather extracts an error of from 1 per cent. to 2 per cent., expressed as a loss of the Epsom Salts, can be expected. Extreme precautions were used, all the charges of the leather were weighed out at the same time and the Epsom Salts solution was added from a 10 cc. burette graduated in 1/20 cc.

It will be noticed that the average loss of the Epsom Salts from the moisture and water solubles determination was practically the same, being 39.9 per cent. and 39.2 per cent., which would indicate that the water of crystallization of magnesium sulphate not accounted for in the moisture determination is included and consequently compensated for in the total solubles figures. These data are simply a confirmation of what one would naturally expect and were anticipated by Parker and Paul (*J. A. L. C. A.*, 1910, 305-316) and by Alsop (*J. A. L. C. A.*, 1915, 78-79), but none of these authors give any figures on the subject. Parker and Paul state that "The amount of water included as mineral matter in the water soluble does not affect the result because the water of crystallization is included as moisture and the water of constitution is the same in the original leather after drying as in the dry soluble matter since the drying is done at the same temperature." They should have added "and for the same length of time," for as shown by the following figures the loss on heating Epsom Salts does not quickly become constant or in other words all of the water of crystallization is not driven off within a reasonable time. This fact is an argument for the drying of the charges for water solubles and moistures under exactly the same conditions.

The losses stated here are the averages from closely agreeing duplicates obtained by heating portions of the finely pulverized salt in the combined evaporator and dryer at 98°-100° C. for the periods given:

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Hours heating	Per cent. loss
16	36.48
20	37.08
36	40.42
40	40.85
56	41.95
72	42.35

Continued heating for 80 hours more, weighing every 16 hours showed practically no further loss, the values obtained ranging from 42.37 per cent. to 42.47 per cent. Portions of the same sample of salt when heated in an electric oven for 16 hours lost at 100°-101° C. 37.02 per cent.; and at 103°-105° C. 39.32 per cent.

In conclusion it is desired to thank Mr. J. S. Rogers for his voluntary offer of co-operation. Mr. Rogers has suggested that there be included in the committee work of the coming year the determination of magnesium directly in the water extract without ashing it and that a comparison be made of the volumetric and gravimetric determination of magnesium.

DETERMINATION OF GLUCOSE IN LEATHER—1920 COMMITTEE REPORT.[1]

By J. S. Rogers, Chairman.

The Committee on leather analysis suggested the following lines of work:

"(*a*) To determine the best concentration of solution, particularly with reference to whether or no stronger solutions than at present used would be advantageous.

"(*b*) Work upon the loss of sugar by fermentation from the standing solutions for a varying length of time.

"(*c*) The influence of the amount of potassium oxalate used upon the determination, and whether or no potassium oxalate is the best agent, and if not what is better.

"(*d*) As to the method of hydrolysis, can the present method be improved?

"(*e*) Relative to the neutralization of solution after hydrolysis, and whether or no sodium carbonate or sodium hydrate is preferable, work having been done which seems to prove that under ordinary procedure sodium carbonate gives inaccurate results, particularly with leather containing salts."

[1] Read at the annual meeting at Atlantic City, May 29, 1920.

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Work has been done along the following lines:

1. Loss of sugar by fermentation of the leather extract.

2. Neutralization of the solution after hydrolysis—Na_2CO_3 compared with NaOH.

3. Neutralization after hydrolysis—with varying amounts of NaOH.

4. Variation in the concentration of leather extract incidentally including a variation in the amount of potassium oxalate.

The sample of leather used was tanned by a combination of oak and chestnut liquors and contained no added sugar or salts. The dextrose sent out with the sample was Merck's, highest purity, anhydrous dextrose, which showed on analysis 97.5 per cent. dextrose.

Results were received from:

R. W. Frey, Leather & Paper Laboratory, Washington, D. C.

L. A. Cuthbert, Elk Tanning Company, Ridgway, Pa.

The following directions were sent out:

General Directions Regarding Committee Work.—Fehling's solutions should be prepared and allowed to stand several days (5 to 7) and then filtered through asbestos. A blank determination should be made on the Fehling's solutions used, using 50 cc. of distilled water in place of a sugar solution. The blank obtained should never exceed one milligram and the crucibles used should be constant in weight after filtering 100 cc. of hot Fehling's solution. The burners used, should be regulated so that the mixed solutions are brought to 100° C. in four minutes (this time should not vary more than 10 seconds in either direction). The solutions should then be boiled exactly two minutes and filtered at once through the prepared Gooch crucibles.

In preparing the solution for analysis the work should proceed without interruption from the beginning of the clarification until the acid is added for hydrolysis. It may then stand overnight before or after boiling if necessary. After neutralization it should then be at once continued to completion.

In all clarifications, unless otherwise specially directed, use a saturated solution of neutral lead acetate for the removal of tannin, and five grams of solid potassium oxalate for precipitation of the excess lead.

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SECTION NO. 1: LOSS OF SUGAR BY FERMENTATION OF THE LEATHER EXTRACT.

Extract 30 grams of the leather sample by the regular Official Method, add 2.4616 grams of the C. P. Dextrose sent out with the leather, make to volume as per Official Method, and mix thoroughly. Transfer to two one-liter flasks marked Nos. 1 and 2 and to solution No. 2 add 5 drops of toluol, mix thoroughly and stopper.

(*a*) Proceed immediately with the regular determination of glucose by the regular Official Method on solutions Nos. 1 and 2, making one clarification, one hydrolysis, and duplicate reductions, stopper and reserve flasks Nos. 1 and 2 at laboratory temperature as soon as the portions have been removed for clarifications.

(*b*) Twenty-four hours after starting (*a*) start and run a second set of determinations on solutions Nos. 1 and 2 as directed under (*a*).

(*c*) Forty-eight hours after starting (*a*) start and run a third set of determinations on solutions Nos. 1 and 2 as directed under (*a*).

(*d*) Seven days after starting (*a*) start and run a fourth set on solutions 1 and 2 as directed under (*a*).

Note and record the range of temperature of the laboratory in which the solutions have been standing during the period between the time of extraction and analysis.

SECTION NO. 2: NEUTRALIZATION OF THE SOLUTION AFTER HYDROLYSIS; Na_2CO_3 COMPARED WITH NaOH.

Extract 30 grams of the official leather sample by the regular Official Method, dilute to two liters and mix. Prepare four 500 cc. volumetric flasks, numbered 1 to 4. In flask No. 2 place 0.6154 gram of dextrose sent out with the leather sample. In flask No. 3 place 0.525 gram $MgSO_4 7H_2O$, and in flask No. 4 place 0.6154 gram of dextrose and 0.525 gram $MgSO_4 7H_2O$. Fill flasks Nos. 2, 3 and 4 to the mark with the leather extract and mix, and place the remainder of the leather extract in flask No. 1. Proceed at once with clarifications following the Official Method up to the point of neutralization of the solutions after hydrolysis, making

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the clarifications and hydrolyses in duplicate on each of the four solutions.

(*A*) *Neutralization With* Na_2CO_3.—Prepare a strong solution of Na_2CO_3 nearly saturated so that not more than 10 cc. are required to neutralize the 5 cc. HCl used for hydrolysis. Neutralize one of the duplicates of each of the four solutions with this Na_2CO_3 solution, running it in from a burette and using litmus paper to show the end point.

(*B*) *Neutralization With NaOH*.—Prepare a strong nearly saturated solution of NaOH so that not over 10 cc. are required to neutralize 5 cc. of conc. HCl.

Neutralize the second duplicate of each of the four solutions with this NaOH solution, running it from a burette, using litmus paper or a drop of phenolphthalein to show the end point.

Proceed immediately from this point with the regular Official Method, running duplicate reductions on each of the eight solutions.

Solution 5.—Weigh out 0.6154 gram of the dextrose sent out and place in a 500 cc. volumetric flask and make to volume with distilled water, clarify using 7.5 grams of potassium oxalate to remove the lead, and hydrolyze in duplicate according to the Official Method. Neutralize one duplicate by (*A*) Na_2CO_3 and the other by (*B*) NaOH and make duplicate reductions.

SECTION NO. 3: NEUTRALIZATION OF THE SOLUTION AFTER HYDROLYSIS; WITH VARYING AMOUNTS OF NaOH.

Extract 30 grams of the leather sample by the Official Method, make to volume and mix. Prepare two dry one-liter volumetric flasks, Nos. 1 and 2. In flask No. 2 place 1.2308 grams of the dextrose sent out and 1.05 grams of epsom salts. Fill the flask to the mark with the prepared leather extract and mix. Place the remainder of the extract in flask No. 1.

The following treatment is to be applied to solutions Nos. 1 and 2: Make four clarifications and hydrolyses by the regular procedure up to the point of neutralization after hydrolysis. Neutralize the four solutions as follows, using one drop of phenolphthalein or litmus paper.

(*a*) Make distinctly alkaline by adding concentrated NaOH solution used in section two, from a burette. Bring back to acid

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reaction with a few drops of HCl, then make just alkaline in reaction by adding N/2 NaOH from a burette.

(*b*) Neutralize as in (*a*) then add 1 cc. of N/2 NaOH in excess.

(*c*) Neutralize as in (*a*) then add 2 cc. of N/2 NaOH in excess.

(*d*) Neutralize as in (*a*) then add 4 cc. of N/2 NaOH in excess.

From this point proceed with the determination by the regular procedure, making duplicate reductions on each of the eight solutions obtained.

SECTION NO. 4: EFFECT OF VARIATION IN THE CONCENTRATION OF LEATHER EXTRACT.

Concentration (A).—Extract 30 grams of the sample sent out by the official method and dilute to two liters.

Concentration (B).—Extract 60 grams of the sample sent out by the official method and dilute to two liters.

In the extraction preparing the concentration *B*, if the leather extractor used will not readily accommodate the amount of leather sample specified without packing, use two extractors, dividing the sample equally, regulating the flow of water so as to deliver one liter to each in three hours, and combine the extracts to make two liters.

Each of the two concentrations prepared as described above is to be treated as follows: except that in concentration *B* use twice as much dextrose and epsom salts as in *A*, thus corresponding with the concentrations of leather extract.

Prepare four 500 cc. volumetric flasks, Nos. 1 to 4. To No. 2 add 0.6154 gram of dextrose sent out with the leather sample. To No. 3 add 0.525 gram $MgSO_4 7H_2O$. Make flasks Nos. 2, 3 and 4 to volume with the leather extract already prepared, and place the remainder of the extract in flask No. 1. Mix the contents of the four flasks thoroughly, and proceed at once with the clarification.

Make duplicate clarifications and hydrolyses by the official method on each of the four solutions up to the point of neutralization of the solution after hydrolysis. Neutralize one of the duplicates as directed under section 3-C of the directions already sent.

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After neutralization proceed at once with the reductions following the official method and making duplicate reductions on each of the eight solutions.

SECTION No. 1.

The results of the work on Section No. 1 are given in Table No. I.

Mr. R. W. Frey gives results obtained on a third (No. 3) solution, treated as in Section No. 1 except that it was put up in four 250 cc. flasks, 5 drops of toluol being added to each, so as to form a layer in the neck of the flask. The averages of these results are as follows:

	Per cent.
Analyzed immediately	8.98
After 24 hours	9.03
After 48 hours	8.92
After 7 days	8.89

He considers this procedure preferable to that given in Section No. 1.

The following comments were made by the collaborators:

FREY: "While conclusion cannot safely be drawn from one set of results, the indications are that conditions for Solution No. 3 prevented any loss of sugar for seven days, while there was appreciable destruction of sugar in Solution No. 2. It was also somewhat surprising that Solution No. 1 showed little if any loss of sugar for the first 48 hours."

CUTHBERT: "The addition of 5 drops of toluol to the leather extract will preserve the solution satisfactorily without change at ordinary room temperature for five to six days; whereas a similar solution without the addition of toluol will begin to lose its glucose content after the second or third day, when kept under the same conditions as to temperature."

CHAIRMAN: The results on Section No. 1 show that there is a loss of sugar in leather extracts standing at laboratory temperatures. This loss was small during the first 48 hours, but increased to a considerable amount at the end of seven days. The addition of 5 drops of toluol per liter and mixing aided materially in retarding the loss. In one case, however, even in the presence of toluol there was an appreciable loss at the end of a week. Both solutions showed mould growth at the end of seven days. The

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SECTION I, TABLE I.—Loss of Sugar by Fermentation of the Leather Extract

	Leather extract plus glucose				Leather extract plus glucose plus toluol				
	Analyzed				Analyzed				
	(1) At once	(2) After 24 hours	(3) After 48 hours	(4) After 7 days	(1) At once	(2) After 24 hours	(3) After 48 hours	(4) After 7 days	Range in degrees C.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
R. W. Frey	9.04 9.00 Av. 9.02	8.83 8.84 8.84	8.94 8.86 8.90	7.90 7.83 7.87	9.01 9.01 9.01	8.92 8.86 8.89	8.99 8.95 8.97	8.47 8.53 8.50	(1) 24–26 (2) 22–26 (3) 22–26 (4) 22–26
L. A. Cuthbert ..	9.36 9.22 Av. 9.29	9.14 9.12 9.13	9.18 9.06 9.12	8.38 8.46 8.42	9.28 9.22 9.25	9.14 9.16 9.15	9.16 9.20 9.18	8.96 9.18 9.07	(1) 20–23 (2) 17–23 (3) 17–23 (4) 16–23
J. S. Rogers.....	9 08 9.08 Av. 9.08	9.20 9.08 9.14	9.10 9.03 9.07	7.67 7.66 7.67	9.17 9.08 9.13	9.15 9.07 9.11	9.15 9.27 9.21	8.98 9 07 9.03	(1) 24–25 (2) 24–27 (3) 22–27 (4) 20–31
General averages	9.13	9.04	9.00	7.99	9.13	9 05	9.12	8.87	
Average loss		0.09	0.13	1.14		0.08	0.01	0.26	

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Chairman believes that the use of toluol as described will preserve leather extracts satisfactorily for at least three days at laboratory temperatures.

SECTION NO. 2.

The results of the work on Section No. 2 are given in Table II. In the first series of results by Mr. Frey, the solutions were just neutralized and were carried through this stage in two groups, one of six and the other of four, so that the last solution in each group had been neutralized sometime before reduction. In the second series of results the solutions were made neutral and 0.3 cc. of alkali added, and each solution was reduced immediately after neutralization.

In the analyses by Mr. Cuthbert and the Chairman, a little excess of NaOH was used, sufficient to cause the precipitation of the magnesium. No record was kept of this excess.

Results obtained by determining the Cu in the Cu_2O precipitates by the Lowe Volumetric Method (*Bur. of Chem. Bul.*, 107 Rev.) of the second series of Mr. Frey's results were given. The average of these results are shown in Table II-A.

TABLE II-A.

Solution	Neutralized Na_2CO_3 Per cent.	With NaOH Per cent.
No. 1	1.07	0.64
No. 2	9.05	8.27
No. 3	0.93	0.89
No. 4	9.10	8.74
No. 5	8.05	7.74

These results are interesting since they show that theoretical results can be obtained by neutralization with Na_2CO_3 if the Cu of Cu_2O precipitates be determined volumetrically.

Mr. Frey gives results obtained by clarifying and hydrolyzing a water solution of glucose by the official procedure and neutralizing by adding varying amounts of concentrated NaOH. The theoretical percentage on a leather basis was 8 per cent. The averages of the percentages found are given in Table II-B.

TABLE II-B.

	Per cent.
Just neutralized	7.83
0.5 cc. excess	7.78
3.0 cc. excess	7.76

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SECTION 2, TABLE II.—NEUTRALIZATION OF THE SOLUTION AFTER HYDROLYSIS, Na_2CO_3 COMPARED WITH NaOH

	(A) Neutralization with Na_2CO_3					(B) Neutralization with NaOH				
	Leather extract				Water soln. of glucose	Leather extract				Water soln. of glucose
	Alone	+ 8% Glucose	+ 7% Epsom salts	+8% Glucose +7% Epsom salts		Alone	+8% Glucose	+7% Epsom salts	+7% Epsom salts & 8% glucose	
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
R. W. Frey	1.00 0.94 Av. 0.97	8.98 8.98 8.98	1.02 1.02 1.02	9.48 9.58 9.53	8.04 8.00 8.02	1.02 0 92 0.97	8.56 8.52 8.54	0.76 0.94 0.85	9.64 9.54 9.59	7.84 7.80 7.82
	1.06 1.06 Av. 1.06	9 10 9.04 9.07	1.02 1.08 1.05	9.58 9.60 9.59	8.04 8.08 8.06	0.54 0.62 0.58	8.30 8.30 8.30	0.90 0 84 0.87	8.80 8.74 8.77	7.72 7.74 7.73
L. A Cuthbert	1.24 Av. 1.24	9.34 9.16 9 25	1.74 1.78 1.76	9.84 9.86 9.85	8.10 8.22 8.16	1.18 1.20 1.19	8.86 8.88 8.87	1.08 1.08 1.08	8.76 8.74 8.75	7.98 7.86 7.92
	1.36 1.26 Av. 1.31	9.24 9.22 9.23	1.74 1.78 1.76	9.70 9.76 9.73	8.18 8.08 8.13	1.02 1.12 1.07	8.86 8.72 8.79	1.08 0.96 1.02	8.72 8.86 8.79	8.12 7.96 8.04
J. S. Rogers	1.17 1.08 Av. 1.12	9.20 9.12 9.16	1.40 1.60 1.50	9.66 9.64 9.65	8.02 7.98 8.00	0.98 0.99 0.98	8.64 8.66 8.65	0.91 0.92 0.91	9.10 9 13 9.12	7.88 7.90 7.89
Maximum	1.36	9.34	1.78	9.84	8.22	1.20	8.88	1.08	9.64	8.12
Minimum	0.94	8.98	1.02	9.48	7.98	0.52	8.30	0.76	8.72	7.72
General avg.	1.14	9.14	1.42	9.67	8.07	0.96	8.63	0.95	9.00	7.88
Avg. ± error		0.00	+ 0.28	+ 0.53	+ 0.07		— 0.33	— 0.01	+ 0.04	— 0.12
Greatest difference	0.42	0.36	0.76	0.38	0.24	0.66	0.58	0.32	0.92	0.40

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These results although below the theoretical do not decrease regularly with increasing amounts of NaOH.

Mr. Frey also gives results of determination made on a pure sample of dextrose showing the following analyses: specific rotation ÷ 52.3, H_2S metals absent, Ca approx. 0.025 per cent, Ba absent, Cl trace. Two solutions were prepared each containing 0.615 gram of the dried dextrose per 500 cc. Clarifications and hydrolyses were made by regular procedure, and neutralization by Na_2CO_3 and NaOH. Blanks on Fehling's solution, water, Na_2CO_3 and NaOH were nil. The results are given in table II-C.

TABLE II-C.

Theoretical recovery of dextrose	41.0 mg.	± error
Averages with Na_2CO_3 of solution (1)	40.0 mg.	—1.0 mg.
Averages with Na_2CO_3 of solution (2)	40.5 mg.	—0.5 mg.
Averages with NaOH of solution (1)	40.3 mg.	—0.7 mg.
Averages with NaOH of solution (2)	40.2 mg.	—0.8 mg.

COMMENTS ON RESULTS OF SECTION NO. 2.

R. W. FREY: "The data in Table II shows that neutralization with Na_2CO_3 gives results considerably too high when glucose and epsom salts are both present in the same solution. It is very disconcerting to note, however, that such was not found to be the case when epsom salts only was added.

The effect of magnesium on the determination of sugar by the reduetion method, using NaOH for exact neutralization, has been brought to our attention by Mr. H. A. Lepper of this Bureau, who found while working with coffee that the interference of magnesium and iron was often so great as to make it necessary to resort to volumetric or electrolytic methods for correct results. (See *Proceedings of The A. O. A. C.*, Report on Tea and Coffee, Nov. 21, 1916.) Mr. Lepper found that a slight excess of NaOH in neutralizing would remove most of the magnesium and iron but he did not consider the excess of NaOH advisable because of the possible modification thereby of the sugars, as frequently mentioned in Browne's Handbook of Sugar Analysis.

Table II also shows that neutralization with NaOH gives generally lower results than with Na_2CO_3, and also that the results with NaOH are not consistent even with the same operator, while they are extremely so for Na_2CO_3. A slight excess of NaOH gives in most cases lower figures than does just neutralizing; such is not the case with Na_2CO_3, as will be seen by comparing

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the first and second series in Table II. For solution No. 4 it will be observed that just neutralizing with NaOH did not remove the magnesium.

It was thought that probably the neutralization ordinarily was carried further in the case of NaOH, and as a consequence that the alkaline conditions for reduction might be appreciably affected or that the excess of alkali might be destroying sugars. The figures in Table II-B, while lower than the theoretical 8 per cent., show conclusively that if NaOH is exerting such influences, the effect is not proportionate to the amount in excess. Incidentally, these results confirm those for Solution No. 5, Table II.

The figures in Table II-C add to the perplexity of the entire data since they show that with pure dextrose neutralization, with either Na_2CO_3 or NaOH gives practically theoretical results, which would indicate that the committee sample was not pure dextrose.

It has long been recognized that the gravimetric determination of sugar, in other than pure solutions, is simply a short-cut at a sacrifice in accuracy. If very accurate results are considered essential, it is suggested that sugars in leather be determined by carrying out the method as now prescribed through to the filtering off and washing of the Cu_2O and then determine the Cu in the Cu_2O residues by the Lowe Volumetric method, which method is both practicable and accurate. Should it be decided that this would mean an unwarrantable amount of work for the determination in mind, then it is felt that slight over-neutralization with NaOH should be substituted for Na_2CO_3 in the present method.

L. A. CUTHBERT: My results in this section indicate that neutralization by Na_2CO_3 gives high results due to the fact that in a leather extract containing magnesium all of the magnesium is not precipitated out by the Na_2CO_3 and a part is precipitated with the copper precipitate, making these results higher. I determined the magnesium present in two of the copper precipitates and found that the high results were due to the additional magnesium present. On the other hand, I found that neutralization by NaOH seemed to give me slightly lower than the theoretical results. In all cases after neutralizing with NaOH a precipitate could be seen in the flask; this precipitate when analyzed proved to be mostly magnesium. After neutralizing with Na_2CO_3, however,

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no precipitate, except in a very few cases, could be seen and the only indication of any precipitation was obtained when filtering. I attribute the high results when neutralizing with Na_2CO_3 to the fact that Na_2CO_3 does not precipitate out all of the magnesium and that this magnesium remaining in solution is precipitated with the copper.

In solution No. 5 of this section, I found the 5 grams of potassium oxalate was not sufficient to neutralize the lead present. Using 5 grams, 6 grams and 7 grams of potassium oxalate, I found 8.16 per cent., 8.04 per cent. and 8.03 per cent. glucose respectively, neutralizing with NaOH. Determinations on this solution without clarification and precipitation with potassium oxalate gave 8.08 per cent. neutralized with NaOH and 8.09 per cent. neutralized with Na_2CO_3.

I dissolved the copper precipitates found in solutions 3 and 4, 1st set, in HCl and found magnesium present in both. The magnesium was determined and found to be 0.86 per cent. and 1.08 per cent., respectively, calculated as $Mg(OH)_2$.

CHAIRMAN: The results from Section No. 2, when averaged, are somewhat misleading in the case of neutralization with NaOH, due apparently to greater or less excess of NaOH being used. The percentages of sugars found have been corrected for the sugar found in the original leather extract and have been plotted to show the effect of neutralization with Na_2CO_3 as compared with NaOH.

These curves are shown on page 425.

No. 1 shows results with 8 per cent. glucose and Na_2CO_3.
No. 2 shows results with 8 per cent. glucose and NaOH.
No. 3 shows results with 8 per cent. glucose and 7 per cent. Epsom salts and Na_2CO_3.
No. 4 shows results with 8 per cent. glucose and 7 per cent. Epsom salts and NaOH.

These curves show NaOH to give low results in all cases except the results by Frey, where he apparently used less alkali than the others.

SECTION NO. 3.

The results obtained in Section No. 3 are given in Table III. The variation shown by the different collaborators is probably due to difficulty in determining the alkaline end point after making the solution acid.

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SECTION 3, TABLE III.—NEUTRALIZATION OF THE SOLUTION AFTER HYDROLYSIS, WITH VARYING AMOUNTS OF NaOH

	Leather Alone				Leather + 8% glucose + 7% Epsom salts			
	A Just alkaline	B Alkaline + 1 cc. N/2NaOH	C Alkaline + 2 cc. N/2NaOH	D Alkaline + 4 cc. N/2NaOH	A Just alkaline	B Alkaline + 1 cc. N/2NaOH	C Alkaline + 2 cc. N/2NaOH	D Alkaline + 4 cc. N/2NaOH
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
R. W. Frey	1.08 1.02 Av. 1.05	1.02 0.86 0.94	0.98 1.00 0.99	0.98 0.76 0.87	9.56 9.64 9.60	9.64 9.54 9.59	9.38 9.34 9.36	9.00 9.04 9.02
L. A. Cuthbert	1.12 1.14 Av. 1.13	1.08 1.00 1.04	1.06 1.20 1.13	1.26 1.22 1.24	9.66 9.74 9 70	9.40 9.60 9.50	9.38 9.66 9.52	9.18 9.06 9.12
J. S. Rogers	1.12 1.11 Av. 1.11	1.04 1.13 1.08	0.90 1.08 0.99	0.85 1.11 0.98	9.50 9.43 9.47	9.51 9.51 9.51	8.96 8.88 8.92	8.82 8.80 8.81
	0.96 1.25 Av. 1.10	1.02 0.90 0.96	0.96 0.98 0.97	0.91 1.01 0.96	9.89 9.78 9.84	9.40 9.22 9.31	9.20 9.22 9.21	8 78 8.66 8.72
Maximum	1.25	1.13	1.20	1.26	9.89	9.64	9.66	9.18
Minimum	0.96	0.86	0.90	0.76	9.43	9.22	8.88	8.78
General average	1.09	1.00	1.02	1.01	9.65	9.48	9.25	8.92
± Error	—	—	—	—	+ 0.56	+ 0.48	+ 0.23	— 0.09

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Mr. Frey gives results by the Lowe Volumetric method on solution No. 2 neutralized by methods *C* and *D*. The average of these results for method *C* are 9.10 per cent. and for *D* 9.04 per cent, thus showing that some Mg is present in the Cu_2O precipitate when neutralized by method *C*, but none is present in this precipitate when neutralized by method *D*. He also gives gravimetric and volumetric results on a solution of the Bureau of Chemistry sample of pure dextrose prepared as solution No. 2, neutralized by methods *C* and *D*. The gravimetric determination for method *C* is high, showing Mg in Cu_2O precipitate, while the volumetric determination is close to theory. In method *D* both gravimetric and volumetric are close to the theoretical, indicating that no Mg is in the Cu_2O precipitate.

COMMENTS ON SECTION No. 3.

R. W. FREY: It is felt that it would be preferable after neutralizing with a practically saturated solution of NaOH to add about 0.3 cc. of the same solution in excess, rather than to bring the solution back to a slightly acid condition, then neutralize with N/2 NaOH and add 4 cc. of the last in excess. After once making the solution alkaline, as called for in methods *A* to *D* inclusive, the end point for the second neutralization with N/2 NaOH is not at all sharp.

L. A. CUTHBERT: Results in this section indicate that an excess of NaOH is required in order to obtain complete precipitation of magnesium before reducing with Fehling's solution. In solution No. 1 (leather extract alone) the results are uniform. In solution No. 2 (glucose and salts added) the precipitation is incomplete when made just alkaline with N/2 NaOH; in this case no precipitate was visible in the flask. An excess of 4 cc. N/2 NaOH appears to give the results approaching closest to the theoretical. Copper precipitates in *A*, *B* and *C* sol. No. 2 filtered very slowly and seemed to be slightly gelatinous. The copper precipitate under *D*, sol. No. 2 (4 cc. N/2 NaOH in excess) filtered quickly and was similar to the ordinary copper precipitate.

CHAIRMAN: The results in Section No. 3 show that as the excess of NaOH is increased more and more of the Mg is precipitated and less therefore appears in the Cu_2O precipitate. With the exception of the first set of results in Section No. 3, 4 cc.

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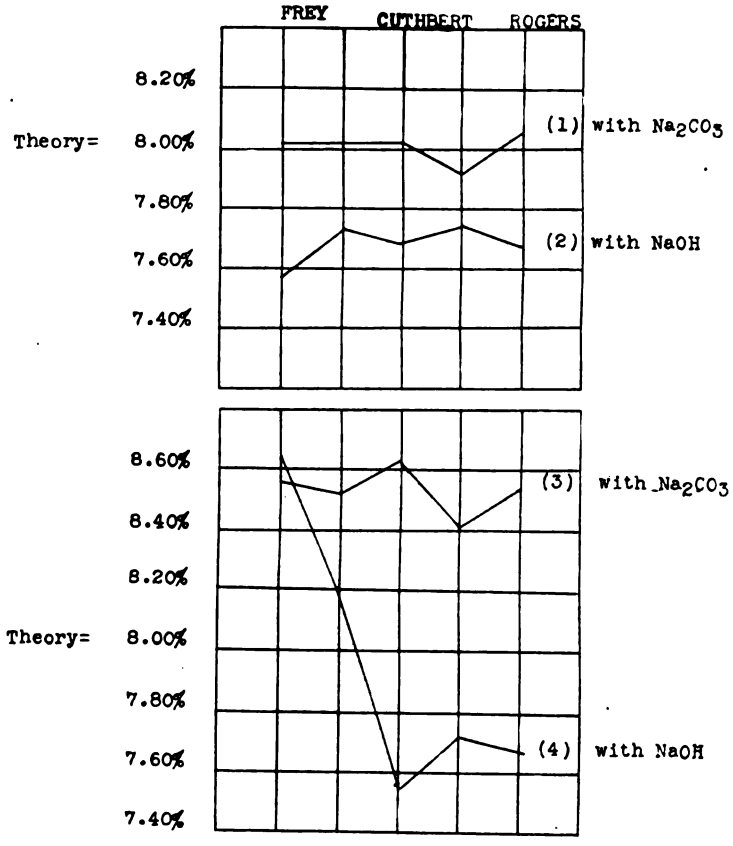
Curves plotted from results in Table II showing the effect of neutralizing with Na_2CO_3 and NaOH. Nos. 1 and 2 leather extract + 8% glucose, Nos. 3 and 4 leather extract + 8% glucose + 7% epsom salts.



excess of N/2 NaOH gives results below 8 per cent. when corrected for the blank on the leather extract. This shows that the Mg has been precipitated and that a second reaction is going on, which causes low results. It is probable that in the presence of different amounts of Mg different amounts of NaOH would be required. These results show further that if NaOH is to remove the Mg so that it will not be precipitated with the Cu_2O, it must be used in excess, since when the solution is just made alkaline, the Mg is not precipitated. These facts are easily seen when the ± errors in Table III are examined.

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Section No. 4.

The results obtained in Section No. 4 are given in Table IV. Concentration *A* (15 g. per liter) is in the first part of the table and concentration *B* (30 g. per liter) in the second part.

Comments on Section No. 4.

L. A. Cuthbert: The concentration of the leather extract appeared to have no effect upon the results, except in the case of solution No. 3 (extract + 7 per cent. $MgSO_47H_2O$). In this solution neutralizing with NaOH, the results were somewhat higher in concentration *B* than those obtained in concentration *A*. The work of this section, however, continued to prove the work of sections 2 and 3. With added $MgSO_47H_2O$, the results were higher than the theoretical and were due, I believe, to the fact that after neutralizing with both Na_2CO_3 and N/2 NaOH the magnesium was not completely precipitated.

From the results of my work, I believe that NaOH should be used for neutralization. The method as described by the Chairman, using an excess of 4 cc. of N/2 NaOH appears to me to give results which approach closest to the theoretical.

Chairman: The results shown in Table IV do not indicate any advantage gained by increased concentration. The concentration involving 30 g. of leather per l. resulted in a larger excess of potassium oxalate being used since more lead was removed with the tannin. There was no indication of a variation in results caused by this excess.

An examination of the plus and minus errors shown in this table shows the excellent results which are obtained by neutralization with Na_2CO_3 in the absence of Epsom Salts, and the high results which are obtained when Epsom Salts are present. They also show good agreement when neutralizing with NaOH in the absence of Epsom Salts, but when Epsom Salts were present, the small excess of NaOH was apparently not sufficient to precipitate the magnesium.

Summarizing the important features brought out in sections 2, 3 and 4, we obtain the following facts. After deducting the blank obtained on the leather extract alone by the different procedures, we find:

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SECTION 4. TABLE IV,—EFFECT OF VARIATION IN THE CONCENTRATION OF LEATHER EXTRACT

15 g. per liter	Neutralized with Na_2CO_3					Neutralized with NaOH			
	Leather Extract					Leather Extract			
	Alone		+ 8% Glucose	+ 7% Epsom salts	+ 8% Glucose + 7% Epsom salts	Alone	+ 8% Glucose	+ 7% Epsom salts	+ 8% Glucose + 7% Epsom salts
L. A. Cuthbert	1.08 1.10 Av.	1.09	9.02 9.24 	1.80 1.80 	9.58 9.64 	1.10 1.10 	9.08 9.18 	1.36 1.52 	9.66 9.64
			9.13	1.80	9.61	1.10	9.13	1.44	9.65
J. S. Rogers	1.21 1.18 Av.	1.19	9.13 9.06 	1.70 1.69 	9.85 9.78 	1.00 0.94 	8.96 8.95 	1.28 1.26 	9.40 9.24
			9.10	1.70	9.82	0.97	8.95	1.27	9.32
Maximum		1.21	9.24	1.80	9.85	1.10	9.18	1.52	9.66
Minimum		1.08	9.02	1.69	9.58	0.94	8.95	1.26	9.24
Average		1.14	9.12	1.75	9.71	1.04	9.04	1.35	9.48
± Error		—	−0.02	+0.61	+0.57	—	0.00	+0.31	+0.44
30 g. per liter									
L. A. Cuthbert	1.06 1.06 Av.	1.06	9.01 9.08 	1.84 1.93 	9.85 9.81 	1.09 1.08 	9.20 9.11 	1.97 2.06 	9.70 9.77
			9.05	1.89	9.83	1.09	9.16	2.02	9.74
J. S. Rogers	1.15 1.09 Av.	1.12	9.03 9.08 	1.89 1.87 	9.85 10.05 	1.02 1.01 	9.14 9.05 	1.80 1.84 	9.97 9.99
			9.05	1.88	9.95	1.01	9.09	1.82	9.98
Maximum		1.15	9.08	1.93	10.05	1.09	9.20	2.06	9.99
Minimum		1.06	9.01	1.84	9.81	1.01	9.05	1.80	9.70
Average		1.09	9.05	1.88	9.89	1.05	9.12	1.92	9.86
± Error		—	−0.04	+0.79	+0.80	—	+0.07	+0.87	+0.81

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A—Neutralization with Na_2CO_3 in the absence of Epsom Salts gives excellent results.

B—Neutralization with Na_2CO_3 in the presence of Epsom Salts gives in most cases high results, Mg being precipitated with the Cu_2O.

C—Neutralization with NaOH, made just alkaline, in the absence of Epsom Salts gives good results.

D—Neutralization with NaOH, made just alkaline, in the presence of Epsom Salts, gives high results, Mg being precipitated with Cu_2O.

E—Neutralizing with NaOH in excess, in the absence of Epsom Salts gives low results in most cases, due to some reaction not yet explained.

F—Neutralization with NaOH in excess, in the presence of Epsom Salts, sometimes gives high, sometimes nearly correct and sometimes low results.

The question then arises, are the low results obtained in some cases, when NaOH is used in excess, caused by NaOH directly or indirectly by some other reaction? In the hope of answering this question, the Chairman conducted the following experiments.

On a sample of pure dextrose prepared by the Carbohydrate Laboratory of the Bureau of Chemistry, the Chairman obtained the results which are given in Table II-D. The solutions used, contained 0.6 g. of dextrose in 500 cc. and received no treatment except the addition of the Na_2CO_3 and the NaOH.

TABLE II-D.

	Mg.	Per cent. leather basis
Theoretical recovery of dextrose.....	40.0	8.00
Water solution of dextrose, untreated....	39.5	7.90
	39.3	7.86
Average	39.4	7.88
Water solution of dextrose.....	39.5	7.90
+ 1 g. Na_2CO_3 in 200 cc.....	39.1	7.82
Average	39.3	7.86
Water solution of dextrose.....	39.3	7.86
+ 1 cc. saturated NaOH in 200 cc....	38.9	7.78
Average	39.1	7.82

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These results show practically no difference and indicate that neither Na_2CO_3 nor NaOH will in themselves cause low results, although there seems to be a very slight tendency toward low results with NaOH.

In order to further compare the effect of neutralization with Na_2CO_3 and NaOH, the Chairman prepared water solutions of three samples of dextrose containing 0.6 g. per 500 cc., clarified, using 7.5 g. of potassium oxalate, hydrolyzed by the regular procedure, and neutralized (*A*) with a considerable excess of Na_2CO_3, (*B*) with 1 cc. excess of conc. NaOH. The sugars used were as follows:

1. A standard sample of pure dextrose from the Bureau of Standards.
2. A sample of pure dextrose from the Bureau of Chemistry.
3. A sample of commercial glucose.

The results are given in Table II-E.

TABLE II-E.

	Mg.	Per cent. leather basis
Theoretical recovery of dextrose on pure samples	40.0	8.00
Bureau of Standards pure dextrose	39.4	7.88
Neutralized with Na_2CO_3	39.0	7.80
Average	39.2	7.84
Neutralized with NaOH	36.4	7.28
	35.8	7.16
Average	36.1	7.22
Bureau of Chemistry pure dextrose	38.9	7.78
Neutralized with Na_2CO_3	38.9	7.78
Average	38.9	7.78
Neutralized with NaOH	35.8	7.16
	35.6	7.12
Average	35.7	7.14
Commercial glucose	30.9	6.18
Neutralized with Na_2CO_3	31.9	6.38
Average	31.4	6.28
Neutralized with NaOH	28.0	5.60
	28.8	5.76
Average	28.4	5.68

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These results indicate that both pure dextrose and commercial glucose clarified by the regular procedure and neutralized with an excess of NaOH give decidedly lower results than when neutralized with an excess of Na_2CO_3. In these analyses, it was noted that the solutions when being neutralized with Na_2CO_3 gave a precipitate, indicating that all of the lead had not been removed, although there was known to be an excess of potassium oxalate present.

In order to determine positively that lead was not being completely removed in the regular clarification, a sample of pure dextrose was weighed out, dissolved and clarified by the regular procedure except that 7.5 g. of potassium oxalate were used to remove the lead, to insure an excess. After removal of the lead oxalate precipitate, HCl was added to the filtrate as for regular hydrolysis. In a few minutes a white precipitate separated. A portion of the original clear filtrate was then tested for lead with H_2S and considerable quantities of lead were found to be present. The lead was not completely removed by potassium oxalate although this reagent was present in excess as shown by testing the filtrate. The formation of a precipitate upon the addition of HCl in the regular procedure has very frequently been noticed. It was supposed that this was lead chloride. In the present Official method, this lead is removed when the solution is neutralized with Na_2CO_3 after hydrolysis.

In order to determine whether or not potassium oxalate was in itself in any way responsible for the low results obtained when NaOH was used in excess, a leather extract with and without the addition of sugar and salts was clarified. The lead was removed with H_2SO_4 and the hydrolysis was made with H_2SO_4. The theoretical amount of dextrose was not recovered. A precipitate was noted in the hydrolyzed solution before neutralizing. After neutralization with an excess of NaOH, the leather extract without sugar and salts was clear and magnesium was precipitated from the solution containing Epsom salts.

Bearing the above data in mind and remembering that lead salts are precipitated by NaOH in the form of $Pb(OH)_2$, which is soluble in excess forming sodium plumbite, Na_2PbO_2, we would expect that when lead is present in the acid hydrolysis solution and this is neutralized by an excess of NaOH, the lead would pass

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into the final sugar solution used for reduction as sodium plumbite.

When the neutralization is made with Na_2CO_3 in excess, the lead is precipitated as the normal or basic lead carbonate and removed from the sugar solution by filtration.

Knowing that lead will enter the complex anion of the tartrates in the same manner in which copper does (*Inorg. Chem.*, Alex. Smith, p. 704), the Chairman believed that the sodium plumbite in the sugar solution in the presence of alkaline tartrates would be reduced in the same manner in which the copper compound is reduced. And knowing that the oxides of lead are in general soluble in excess of caustic alkali, he believed that a part of the dextrose in the sugar solution might be used up in the reduction of sodium plumbite and thus would not give the correct amount of Cu_2O. To determine this point, three solutions of the committee sample of dextrose were prepared as follows:

1. 0.164 g. of dextrose per 200 cc.
2. 0.164 g. of dextrose + water + 1 cc. of concentrated NaOH in 200 cc.
3. 0.164 g. of dextrose + water + (1 cc. of saturated lead acetate + 1 cc. of concentrated NaOH) in 200 cc.

The results showing the effect produced by the presence of sodium plumbite are given in Table II-F.

TABLE II-F.

	Mg.	Per cent. leather basis
Theoretical recovery of dextrose.....	41.0	8.20
(1) Dextrose untreated	39.9	7.98
	39.9	7.98
Average	39.9	7.98
(2) Dextrose + NaOH	39.84	7.97
	39.70	7.94
Average	39.77	7.96
(3) Dextrose + sodium plumbite.....	38.36	7.67
	37.95	7.59
Average	38.15	7.63

The results shown in Table II-F indicate, first, that the committee sample of dextrose is no more affected by an excess of NaOH than are the pure samples from the Bureau of Chemistry

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and Bureau of Standards, and thus tend to disprove the statement that the committee sample might not be pure; secondly, they give further evidence that NaOH even in excess does not of itself cause low results in the determination of glucose.

The results obtained with the solution containing sodium plumbite indicate that its presence in the sugar solution used for reduction causes low results. It is probable that a part of the dextrose is used in reducing the sodium plumbite.

Slightly varying conditions of precipitation may cause greater or less quantities of lead to pass into the hydrolysis solution. The variation in the amount of lead thus remaining unprecipitated doubtless explains the variation in results obtained when NaOH is used in excess. If the lead were completely precipitated, theoretical results should be obtained. The Chairman regrets that the available time did not permit more extended investigations along these lines, and hesitates to draw final conclusions based on so few results. The above explanation, however, seems very plausible.

General Summary.

(1) Results of section No. 1 indicate that 5 drops of toluol per liter will preserve leather extracts at laboratory temperatures for at least three days without material loss of sugar. An average of 1.14 per cent. glucose was lost in leather extracts standing seven days at laboratory temperatures without a preservative.

(2) Results of section No. 2 indicate that when Na_2CO_3 is used for neutralization of the solution after hydrolysis, in the presence of Epsom salts, high results are obtained, due to the precipitation of magnesium with the cuprous oxide.

(3) The use of caustic soda for neutralization of the solution after hydrolysis will result in the precipitation of magnesium, if used in excess.

(4) The results of section No. 4 do not indicate any advantage gained by the use of stronger solutions for analysis.

(5) The results shown in Tables II-D, II-E, and II-F, indicate that the low results obtained in many cases when neutralization was made with NaOH, are not due directly to any action of NaOH on the dextrose, but are due to the action of sodium plumbite, formed when NaOH in excess acts upon the lead which was

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not completely removed from the solution before hydrolysis by precipitation with potassium oxalate. The results of Table II-F indicate that the presence of the sodium plumbite in the sugar solution causes low results.

RECOMMENDATIONS.

(1) Although toluol did not give perfect preservation, it is recommended that it be adopted as a provisional preservative for leather extracts.

(2) For leather extracts which do not contain appreciable quantities of Epsom salts, it is recommended that Na_2CO_3 be retained as the official reagent for neutralization after hydrolysis.

(3) For leather extracts containing considerable quantities of Epsom salts, it is recommended that neutralization be made with a conc. solution of NaOH, using only such excess as is required to precipitate the magnesium, and taking special precautions to make the removal of lead before hydrolysis as complete as possible.

(4) It is recommended that work on the determination of glucose be continued with a view to determining the best method for the removal of lead, and the best conditions for hydrolysis.

ABSTRACTS.

Sulphite Cellulose Extracts. By GEORGES VIE, *Le Cuir*, 9, 160 (1920). The residual liquor resulting from the sulphite digestion of wood in the manufacture of paper pulp may be rendered suitable for use in the tannery by neutralizing and concentrating, but it has no true tanning properties. They should be employed in conjunction with other tanning extracts as skins tanned exclusively with sulphite cellulose are very thin. The best way of making up seems to be to dissolve each extract separately, to mix the warm solution in a special vat and to cool with constant stirring. Sulphite cellulose extract behaves somewhat differently with each kind of tanning extract, but generally causes a marked loss of tannin (according to analysis) in the extract with which it is mixed, and a lower yield and quality of leather. It is best used for retanning because of its decolorizing properties. The author gives a table of results of the analysis of mixtures of sulphite cellulose with chestnut, quebracho, myrobalan and mimosa extracts.

The Treatment of the Warble. By H. PERIGAUD, *Le Cuir*, 9, 158 (1920). The methods of curative treatment of the warble, such as pressure with the fingers, surgical intervention, etc., very often involve serious damage and the results are relatively unsatisfactory. A really

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cheap and effective method used by the author for many years consists in the application of empyreumatic oil. Its odor drives off the warble flies and prevents them laying their eggs on the hairs of the animal, or if the eggs should be deposited they will dry up.

Tanning Value of the Leaves of Pimenta Officinalis. *Bull. Imp. Inst.*, 1919, p. 299. The leaves, examined as a tanning material showed 14.0 per cent. tannin and 7.9 per cent. soluble non-tannin matters, the tintometer readings being, red 9.2, yellow 33.9.

It is suggested that after being steam distilled for the preparation of the essential oil, the residual leaves might be used locally for the preparation of a tanning extract. The leather produced with this material was pale brown, firm and of fairly good texture. *J. S. L. T. C.*

Tan Barks of Western Australia. *Minister of Forests Dept.* Every member of the Eucalypt family contains more or less tannin, but only in a few cases is there sufficient present to warrant the material to be used directly as a tanning material. Others might be used in the manufacture of extracts.

The tannin content of some of the barks is as follows:

	Per cent.
Marri (Redgum) "Kino"	68
Blue Leaf Mallett bark	47
Silver Mallett bark	45
Brown Mallett bark	41
Swamp Mallett bark	36
Round Leaf Moort bark	33
Gimlet-wood bark	26
Spotted Gum bark	24
Blackbutt bark	19
Moort or Territt	16
Black Mangrove bark	46
Red Mangrove bark	44

Black and Golden Wattle have only been introduced into Western Australia to a limited extent, but systematic cultivation is being considered.

With regard to "Marri" (Redgum) *Eucalyptus calophylla* the dark color of the tan is the main objectionable feature of this material, but experiments are in progress to overcome this defect. The "Kino" is collected by scraping the trunk of the tree, but in this direction tapping experiments are in progress.

Mallet bark was exported first in 1903 to the value of £859, but rose to the value of £154,087 in 1905, Germany being the chief customer. In Germany it was made into extract and re-exportetd. *J. S. L. T. C.*

Sant Grains. *Bull. Imp. Inst.*, 1919, 17, p. 246. This is the name given to a material prepared from the sant pods, *Acacia Arabica* of the Sudan. The pods are ground to a powder and the seeds and fibrous matter removed by sifting. Analyses of these grains made at the Imperial Institute show from 55 to 60 per cent. of tannin. Technical trials gave satisfactory

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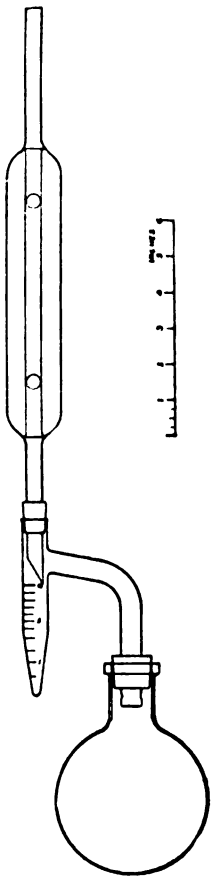
results, being used instead of sumach for finishing skins tanned with bark. Two thousand tons can be produced annually in the Sudan.

J. S. L. T. C.

A Convenient Method for the Determination of Water in Petroleum and Other Organic Emulsions. By E. W. DEAN and D. D. STARK, *J. I. & E. C.*, 12, 486. One hundred cc. of the emulsion to be tested and 100 cc. of solvent is placed in a 500 cc. flask together with a boiling stone. The apparatus as shown in the figure is connected up and heat is applied to the flask until the distillation proceeds at the rate of 2 to 4 drops per second. The distillation is continued until all droplets of water in the flask, distillation tube and condenser have disappeared. The volume of water collected in the graduated receiver is then read off. The solvents for the determination, which gave the most satisfactory results, were so-called cleaners, naphtha and a mixture of 80 per cent. commercial xylene and 20 per cent. commercial benzene. In this determination the solvent must not be saturated with water as there will not be more than 10 cc. of the solvent in the receiver at the end of the distillation. The method has been tried with a number of emulsions prepared by mixing known amounts of water with anhydrous oils and the results checked within ±0.1 cc.



Spent Wattle Bark. *Bull. Imp. Inst.*, 1919, 17, 247. The large quantities of spent wattle bark available have been successfully used in the manufacture of brown paper, cardboard and a cheaper grade of white paper. The difficulty arising from the presence of brown specks—due to a corky layer in the bark—has been studied, and a process has been worked out whereby these can be removed and a better class paper prepared.

J. S. L. T. C.

Simplified Method for the Determination of the Molybdenum Value. By R. LAUFFMANN, *Ledertechn. Rundsch.*, 11, 93-94, 1919; *Chem. Zentr.*, 91, II, 220, 1920. Ten cc. of filtered tannin solution of about four times the usual strength for analysis is mixed with 10 cc. of a reagent composed of equal volumes of 10 per cent. ammonium molybdate and 15 per cent. ammonium chloride solutions and filtered. Ten cc. of the filtrate is evaporated to dryness and dried in the water oven to constant weight. At the same time, 10 cc. of the tannin solution and 10 cc. of the above reagent are evaporated together in a basin and dried to constant weight. The

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weight found by the evaporation of the filtrate is doubled and the product is subtracted from the dry weight of the unfiltered mixture, the difference giving the weight of the precipitate. This is calculated as a percentage of the total dissolved solids of the tannin extract. The following molybdenum values are given: Oak bark extract 65.5-81.3; oak wood extract 112.0-152.1; spruce bark extract 23.6-36.7; chestnut extract 148.2-194.3; quebracho extract, solid, not sulphited 2.0-33.8; the same, fluid, not sulphited 0.0-23.4; mangrove extract 117.9; mimosa bark extract 67.9

J. S. C. I.

Formaldehyde in the Tannery. By B. KOHNSTEIN, *Haute und Lederberichte,* through *Lea. Tr. Rev.,* Apr. 14, 1920. When bacterial colonies in cultural gelatine were placed in a test tube, and the tube was stopped with a pad of cotton wool soaked in formaldehyde, it was found that not only were the bacteria killed, but the gelatine was hardened. A large German chemical firm made a special study of the subject, and hardened gelatine was used for buttons and combs, while formaldehyde solutions were used for the preservation of organic specimens in place of the more volatile and inflammable alcohol. These experiments led to attempts to use formaldehyde as a tanning agent. The first trials were made in connection with the production of white leather. As far back as 1894 it had been established that formaldehyde must be brought into contact with hide substance only in very dilute solutions, and that its action must be limited to a short period, if a hard and brittle product is to be avoided. In order to impart a sufficient degree of softness and elasticity to formaldehyde leathers the tan liquors containing formaldehyde were diluted with glycerine. The purpose of using formaldehyde in making white leather was to make possible the total exclusion of alum, so that glace gloves might be capable of being washed. At that time, however, formaldehyde was a comparatively expensive product, and its use did not seriously threaten that of alum, which was cheap; it was not until afterwards, when the technology of formaldehyde tanning became better known, that it came into more general use.

In order to investigate the nature of formaldehyde tanning, the author conducted researches and found that hides treated with a pure formaldehyde solution give up the formaldehyde after treating them in an autoclave at about 2½ atmospheres pressures, and become again susceptible to the action of acetic acid, and give a gelatinous mass on boiling. The formaldehyde is much more firmly united to the fiber if the hide is treated simultaneously with an alkali. It is evident, therefore, why the glue manufacturer avoids glue stock from hides which have been preserved with salt and formaldehyde. The liming preparatory to unhairing caused formaldehyde tanning proper to take place, and the glue stock is thereby much reduced in value.

It must be laid down at the outset as a guiding principle that the concentration of the formaldehyde in the tanning liquor must not on any account exceed 0.2 to 0.4 per cent., and that the time of action should be limited to one or two days. Pure formaldehyde solutions may be used

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for hardening raw hide for technical uses, or for hardening previously tanned hide intended for sole leather. The formaldehyde must, however, be extracted from the interior of the substance of the hide before tanning with vegetable extracts is continued.

Formaldehyde is also used as a swelling liquor for sole leather. A mixture of hydrochloric acid and formaldehyde is usually chosen. It is, however, usually best to color the hides for one or two days in a liquor of 8 to 12 degrees, and then hang them in the formaldehyde-hydrochloric acid bath. After swelling, which occurs more quickly and evenly if air is blown in between the suspended hides—thereby agitating them slightly and assisting diffusion of the solution—the hides are again treated with a concentrated vegetable tanning liquor. In view of the well-known fact that a hide containing acid is very hard to tan and inclines to become "dead," the hide should, before this further treatment with vegetable tanning material, be suspended in cold water to extract the hydrochloric acid and the excess of formaldehyde.

Formaldehyde can also be used in pickling, for hides intended for chrome tanning. The pickle usually consists of sulphuric acid and salt, or hydrochloric acid and salt, in the proportion of 1 per cent. sulphuric acid or 2 per cent. hydrochloric acid and 10 per cent. salt, calculated on the weight of the hide. But even if a dilute alum solution is used for pickling, weak formaldehyde can be added.

As only basic chrome liquors can be used in chrome tanning, an alkali having to be added to the solution of chromic salt, so also weak formaldehyde solutions can only be used in tanning proper if soda, potash or borax is added; but tanning with formaldehyde may be combined with chrome or alum tanning. Glace finish lamb skins are pegged and treated with an alkaline formaldehyde solution. With alum-dressed glace leather the period of pegging will be longer or shorter in proportion to the length of time the skins have been stored. After the formaldehyde tanning, a dressing will be necessary (egg-yolk and flour). By this procedure a washable leather is obtained. Alkaline formaldehyde solution can be added directly to basic chrome liquors, and the skins are finished off in the mixture in the revolving drum. The addition of glycerine will be found very advantageous in this case.

Formaldehyde can also be used successfully on vegetable-tanned upper leather. The hides, previously tanned in gambier or quebracho are soaked in a weak formaldehyde solution to fix the tanning material. They are then finished off in a liquor of 4° to 6°. This upper leather is very close in grain and substance.

Lyotrope Influence and Adsorption in the Theory of Wetwork. By H. G. BENNETT, *J. S. L. T. C.*, **4**, 75 (1920). The author discusses soaking, liming, puering, bating and drenching from the standpoint of his views advanced in a previous paper on the "Swelling of Gelatin."[1] The changes in volume that occur in a gel are due to either lyotrope influence

[1] This JOUR., **13**, 270.

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or ionic adsorption or a resultant of their forces. There are five independent factors influencing the swelling of a hide gel in an alkaline liquor, namely, (1) the adsorption isotherm of hydroxyl, (2) adsorption isotherm of the cation, (3) lyotrope influence of the undissociated alkali, (4) lyotrope influence of the hydroxyl, and (5) lyotrope influence of the cation. The author's conclusion is that the net adsorption of the hydroxyl ion is the principal factor in alkaline swelling and that the next most important factor is the lyotrope influence of the cation. Explanations are offered of the processes involved in wetwork and phenomena that occur to conform to the author's theory.

The Lactic Acid Industry. By TARIFF COMMISSION, *Chemical Age*, **2**, 373 (1920). Lactic acid, as its name implies, is the chief acid present in sour milk. It is not present in fresh milk, but is formed from the sugar in the milk during the fermentation or souring. It is also present in some other fermented food products, such as sauerkraut. Commercial supplies of lactic acid are not obtained, however, from milk, but by the regulated fermentation of some form of sugar, starch, or other carbohydrate material.

Technical lactic acid is customarily graded according to whether it is light or dark in color and according to its strength—22 per cent., 44 per cent., and 66 per cent. being strengths commonly sold. These grades contain coloring matter and many impurities and usually have an unpleasant odor caused by the presence of some butyric acid. Lactic acid, U. S. P., is a refined article containing not less than 85 per cent. of lactic acid and conforming to the specifications of the Pharmacopœia which insure that, except water, only traces of impurities shall be present.

"Edible" lactic is a refined acid which, however, does not conform to the strict specifications of the Pharmacopœia. It is usually weaker than the U. S. P. grade, has a yellowish color and may contain small amounts of calcium sulphate. It should be free from butyric acid, which is always present in the technical acid, and which has an exceptionally unpleasant flavor.

The technical grades of lactic acid are used chiefly in tanning and dyeing. Hides are usually treated with lime, lime and sodium sulphide, or arsenic sulphide, to remove the hair. These materials are customarily removed from the hide by soaking in the "bran drench." The bran drench is prepared by the fermentation of a mixture of bran and water which yields an acid solution containing lactic, acetic, and butyric acids. Lactic acid or lactic acid mixed with sodium or potassium lactate is now being used by many tanners as a substitute for the bran drench. Lactic acid is used for "plumping" sole leather. Tanners now consume over half the lactic acid produced.

Lactic acid is also used in the dyeing of textiles and leather, especially in the chrome mordanting of wool and as a substitute for acetic acid in dyeing and printing. It has the advantage of being much less volatile than acetic acid, and therefore is less liable to be lost in operations involv-

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ing steaming or boiling. The antimony salt of lactic acid is a competitor of tartar emetic in dyeing, and titanium lactate is used in making leather.

Edible lactic acid has not been marketed extensively, but recent discoveries and commercial developments will probably cause it to be placed on the market in larger amounts and at a lower price. A large market will probably develop for beverages, and lactic acid should prove a serious rival to citric acid for these purposes. Another large prospective use is in the baking industry. It is claimed that the addition of lactic acid or a mixture of lactic acid and sodium lactate to the dough results in a marked improvement in the quality of the bread, especially when wheat substitutes are used. Lactic acid favors a more vigorous yeast fermentation in the dough, which is desirable, and inhibits the undesirable fermentations which sometimes result in the formation of "ropy" bread or "sour" bread. Lactic acid is also used to some extent in the brewing trade.

Lactic acid, U. S. P., and several salts of lactic acid are also used in medicine. It is sometimes prescribed in cases of dyspepsia, diarrhea, croup, cholera, carcinoma, and as a solvent for false membrane. Calcium lactate or calcium lacto-phosphate is occasionally prescribed as a cure for rickets and malnutrition in children. Some medical authorities claim that the habitual consumption of foods or beverages containing lactic acid acts as a preventive of intestinal diseases, such as typhoid fever and cholera.

Various raw materials are used. Glucose, made from cornstarch, gives a "light" product of good quality, but is more expensive than some other materials. Molasses from either cane or beet sugar was formerly the principal raw material, but is now in such great demand for food and for alcoholic fermentation that other cheaper materials are used. Farinaceous materials, such as spoiled corn and potatoes, have been employed.

These require a preliminary treatment by boiling with acid in order to convert the starch into glucose, a variety of sugar. Recently the waste obtained in the manufacture of buttons from vegetable ivory (tagua nuts) has become an important raw material for making lactic acid. This material must be heated with sulphuric acid under pressure to convert it into mannose (another variety of sugar) and the acid must then be neutralized. The sugar solution from any of these sources must be diluted to the proper strength ,and some nitrogeneous plant food, such as corn meal, then added to nourish the micro-organisms responsible for the fermentation.

The manufacture of lactic acid may be considered in three steps: 1st, the preparation of the raw material in a condition suitable for the fermentation; 2d, the fermentation under conditions so regulated as to yield lactic acid primarily; 3d, the conversion of the product into a form suitable for sale and use.

Sugar is fermented by many different organisms yielding different products, such as alcohol, lactic acid, citric acid, butyric acid, glycerine, and acetone. The problem, therefore, is to control fermentation in order to secure the maximum yield of lactic acid and the minimum of other products. This is accomplished not by sterilization of the materials and

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apparatus and subsequent inoculation with a pure culture of the desired ferment, but rather by controlling the temperature and acidity of the liquid. The lactic-acid ferment thrives at a temperature above that at which the other varieties of ferments are able to develop vigorously.

The fermentation process yields much heat; artificial heat therefore is not necessary except at the beginning of the fermentation or in very cold weather. The lactic acid produced tends to stop the process; the acid must therefore be neutralized from time to time by the addition of lime. The fermentation requires about six or eight days. The product is a dilute solution containing calcium lactate, lactic acid, with some butyric and succinic acids, glycerine, coloring matter, and unchanged sugar.

In order to convert this material into a form suitable for sale, the lime must be eliminated by the addition of sulphuric acid. This converts the calcium lactate into lactic acid and calcium sulphate which is insoluble and can be separated by filtration. The resulting liquor is then evaporated in copper vessels to the desired strength, usually 22 per cent. or 44 per cent.

The manufacture of the edible and U. S. P. lactic acid is a more difficult and complex process, the details of which are guarded as trade secrets. The crude fermentation lactic acid is purified either (*a*) by crystallization of some salt (usually the calcium or zinc salt) and then by separation of the free acid, or (*b*) by the distillation of the crude acid with superheated steam in a vacuum still, or (*c*) by the extraction with amyl alcohol or ether. The latter method is usually employed to make U. S. P. lactic acid.

The output of edible lactic acid in the past has been only a small percentage of the output of the technical acid. However, it is reported that manufacturers are planning to increase the production of the pure acid many fold in the near future. There are at least four American companies with well-matured plans to enter this field.

The manufacture and chief uses of lactic acid were developed by Americans. The industry was well established in the United States before the manufacture of lactic acid was undertaken in foreign countries.

The founder of the industry was Charles E. Avery, who built the first lactic-acid factory in Littleton, Mass., in 1881. It had long been known that lactic acid is formed by the fermentation of starch and sugar and that the process always stopped after converting only a small fraction of the sugar into lactic acid. Avery found that the fermentation is stopped by the accumulation of the lactic acid itself and that if the acid is neuralized as formed, the fermentation may be continued until nearly all of the sugar is converted into salts of lactic acid.

Avery at first attempted to market the product in the form of an acid calcium lactate for use in baking powders as a substitute for cream of tartar. This attempt, however, was not successful, owing to difficulties in refining the lactic acid and to unsatisfactory keeping qualities of the baking powder made therefrom. The product was then sold under the proprietary name of "Lactart" as an acid beverage. The original company,

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the Avery Lactate Co., discontinued manufacturing in 1887, and the plant was turned over to the bondholders, who continued the business under the name of the Avery Lactart Co. In 1894, A. A. Claflin, who was connected with the Avery Lactart Co., developed the use of lactic acid in the dyeing of wool with chrome mordants. A technical grade of acid which was comparatively easy to make was satisfactory for the purpose, and a rapid expansion of the industry followed the broadening of the market. Within a few years the manufacturers developed the use of lactic acid in tanning leather as a substitute for the bran drench and as a plumping agent. The tanning industry has since become the largest outlet for lactic acid. As a result of these discoveries the output increased from about 10,000 pounds in 1894 to about 400,000 pounds in 1897.

The Purification of Tannery Wastes. By HARRY B. HOMMON, *Public Health Bulletin No. 100,* U. S. Public Health Service. A detailed report of the experiments described in this JOUR., 12, 307 (1917). The process of treatment recommended is, in general outline, as follows:

Treatment of the spent-tan liquor with lime sludge from the unhairing vats, followed by about 24 hours' quiescent sedimentation.

Mixture of the supernatant from this treatment with the remainder of the wastes and treatment of the combined wastes with copperas (ferrous sulphate), at the rate of about 10 grains per gallon.

Sedimentation of the mixed wastes in a tank having sufficient capacity to permit 24 hour's operation of the filters, and to provide for a minimum time of passage during the daytime of 4 hours.

Preliminary filtration of the settled liquors through cinder roughing filters at about 200,000 gallons per acre per day.

Sedimentation in tanks for about one hour.

Secondary filtration through beds of coarse sand.

Addition of the sludge from the spent-tan liquor treatment to the main sedimentation tank at frequent intervals and withdrawal of the sludge from the latter and from the second sedimentation tank to sludge drying beds as necessary.

Utilization of the dried sludge as a fertilizer.

Direct utilization of the sludge to fertilize near-by land by means of tank wagons may be found more economical than the use of drying beds under certain conditions.

The capacities and rate of operation of these various treatment devices will vary with the requirements of the individual case, especially as regards the quality of the final effluent necessary.

In Appendix I is given data for the design of a plant for the treatment of the wastes resulting from the tanning of 100 hides per day, under conditions that require a non-putrescible effluent but permit the discharge of considerable color, the most frequently occurring conditions. To meet other requirements, the designing engineer will find it advisable to study the detailed experimental work given in the body of the report.

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In addition to the bibliography as given in this JOUR., **6**, 464 (1911), by P. A. Esten, Bibliography of Tannery Waste Treatment, the following is given:

1865—Royal Commission on Rivers Pollution. First report, p. 22; third report, p. 35.

1868—Royal Commission on Rivers Pollution. First report, pp. 37 and 103.

1898—Dibdin, Wm. J., and Thudicum, George. *J. S. C. I.*, **17**, 315.

1902—Dunbar and Thum. Beitrage zum derzeitigen Stande der Abwasserreinigungsfrage, p. 140. R. Oldenbourg, Munich and Berlin, 1902.

1909—Clark, H. W. Disposal and Purification of Factory Wastes. 41st Ann. Rep. Mass. State Board of Health.

1910—Carnegie Tech. 1910. Sewage Disposal and Treatment. (Bibliography, including industrial wastes.)

Mass. State Board of Health, 1910. Experiments on Purification of Tannery Wastes.

1911—*Leather Trades Review*, 1911, vol. 44. Pollution of Rivers by Discharge of Tannery Wastes.

Morrison, J. A. S. The Chemical Examination of Waters and Trade Effluents. This JOUR., **6**, 544 (1911).

Study of the Pollution of Rivers by the Discharge of Residuary Waters from Tanneries. Report by the Syndicat general des Cuirs et Peaux de France, *Lea. Tr. Rev.*, **44**, 874.

1912—Alsop, E. C. Purification of Liquid Tannery Wastes by Forced Oxidation. This JOUR., **7**, 72 (1912).

Purification of Tannery Wastes. *J. S. C. I.*, 1912.

Purification of Tannery Effluents. *Lea. World*, **4**, 119. (r) This JOUR., **7**, 243.

Appelius, W. The Purification of Waste Waters from Tanneries. (a) This JOUR., **7**, 346, from report of Freiburg Tanning School, 1911-1912.

Loveland, F. A. Tannery Sewage Disposal. *S. & L. Rep.*, July 18, 1912. (r) This JOUR., **7**, 474.

Foster, J. British Patent No. 2,190. May 1, 1912.

The Purification of Tannery Effluents. *La Halle aux Cuirs*, Parte Technique, June, 1912, pp. 81-90; *Lea. Tr. Rev.*, **45**, 752.

1913—Veitch, F. P. The Purification of Tannery Effluents. This JOUR., **8**, 10-22.

Duyck, M. Tannery Effluents. *La Halle aux Cuirs*, p. t., Feb. 9, 1913. (a) This JOUR., **8**, 168.

Leather Trades Review, 1913, vol. 8. Purification of Tannery Wastes.

Jettmar, J. Tannery Effluents and Their Treatment. *Collegium*, 1913, 5-9. (a) This JOUR., **8**, 229.

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Phelan, J. W., and Cohen, J. H. Valuation and Fixation of Tannery Effluents. This JOUR., 8, 426-438

Healy, H. W. Tannery Refuse as a Fertilizer. *Rural New Yorker*, May, 1912. (r) This JOUR., 8, 438.

Further Studies on Purification of Tannery Waste. Mass Board of Health, 1913.

1914—Trade Waste at Stockton, Cal. In connection with sewage disposal, *West. Eng.*, April, 1914.

Garcon, Jules. Tannery Effluents and Their Purification. *Bull. Soc. d'Encourgement*, 121, 62-65. (a) This JOUR., 9, 191.

Rolants, E. Purification of Tannery Sewage. *Le Marche des Cuirs*, Feb. 26, 1914, p. 104. (a) This JOUR., 9, 195.

Roth, Albert. Disposal of Tannery Waste. This JOUR., 9, 512.

Smoot, C. C. Sewage Disposal and Use of Tannery Waste. This JOUR., 9, 523.

1915—Veitch, F. P. The Purification of Tannery Effluents and the Recovery of By-products Therefrom. This JOUR., 10, 126.

Pearse, Langdon. Treatment of Industrial Wastes. *S. & L. Rep.*, Apr. 22, 1915, p. 49. (r) This JOUR., 10, 293.

Kershaw. *Surveyor*, 47, 93-5 (1915).

Helfrich, John. Recovery of the Sludge from the Sulphide Process of Depilating Skins. This JOUR., 10, 367.

Seltzer, J. M. Sewage Disposal. This JOUR., 10, 370.

Roth, E. The Disposal of Waste Liquor from Industrial Plants. *Vtljschr. off. Gesundh. Pflege*, 47, 129-68; *Chem. Zentr.*, 11, 727, 1915.

1916—Eddy, H. P., and Fales, A. L. The Activated Sludge Process in Treatment of Tannery Wastes. *J. I. E. C.*, 8, 648-51. (r) This JOUR., 11, 441.

Harvey, A. Analysis of Tannery Wastes as Manures. *Coll.* (London), 1916, 151-2.

1917—Jackson, D. D., and Bushwell, A. M. The Sterilization of Tannery Wastes. This JOUR., 12, 56.

Jackson, D. D., and Bushwell, A. M. The Disinfection of Tannery Wastes. This JOUR., 12, 229.

Hommon, H. B. The Purification of Tannery Wastes. This JOUR., 12, 307.

Disinfection of Tannery Wastes by Means of Chlorine. Discussion. This JOUR., 12, 389-395.

Peck, C. Lee. Treatment of Tannery Sewage. This JOUR., 12, 422.

Rohland, P. Colloidal Clay Process for the Effluent of Leather Factories. *Ledertechn. Rundsch.*, 6, 97; *Chem. Zeit.*, 37, 354.

Trotman, Leather Trades Chemistry. C. Griffin & Co., Ltd.

G. W. S.

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Some Unsolved Problems in Leather Making. By J. R. BLOCKEY, *S. & L. Rep.*, Oct. 9 to Dec. 18, 1919. The author discusses the difference between analytical figures and practical behavior of liquors, extracts and tanning materials and states the need of knowing how far the analytical figures are born out in practice. In the analysis of extracts, the amount of insolubles found by the official method does not compare with that found in practice. Besides the ordinary insolubles there is the "bloom" obtained from certain materials—what is the cause of the production of bloom and the easiest means of preventing it ? Moreover what is the function of insoluble matter in a tan liquor ? How far tannery conditions vary from the ideal or how much tannin, as found by analysis, is actually used in the tannery is a problem about which little is known. How much of the available tannin is in the final leather ? The commonest control method for the estimation of acid in liquors, measures only one function of the acid, namely, its lime neutralizing value. Unrestricted fermentation of the tan liquors besides producing acid, destroys tannin probably in large quantities and the author advocates the use of sterile liquors and thinks it would not be impossible to discover an extremely effective antiseptic which would keep the liquors sterile without detriment to the leather.

Temperature is characterized as one of the factors which has the most influence on the processes of tanning but about which little is known. What is the optimum temperature for each step in tanning ? With tanning materials the temperatures at which the maximum amount of tannin is extracted, have been determined, which resulted in considerable gain to the tanners. With lime liquors attempts are made to equalize the conditions due to changes in temperature by using, in winter, either older liquors or larger quantities of sulphide, for bacterial action is evidently checked at the lower temperatures. Fermentation in the tan liquors is influenced by differences in temperature and so is drenching and swelling. According to Procter's theory there will be less swelling at higher temperatures and more at lower. Some points of great importance are the influence of temperature on the speed of penetration of the tan liquor; the final weight of leather, and the firmness and quality.

Finished leather presents many unsolved problems, for example, is cracky sole leather inferior from a wearing point of view ? What is the cause of a cracky leather and what is the relationship between brittleness and wearing properties ? It cannot be crackiness itself which is the cause of the supposed inferiority from a wearing point of view, as crackiness as a rule only applies on the grain and may be overcome by simply buffing it. The author concludes by attacking the universal demand for good color in sole leather and claims that tanners are forced to resort to processes which result in deterioration in the quality of the leather and which add materially to the cost of production in order to obtain a good color. G. W. S.

Leather Dyeing. By F. KOHL, *Gerber*, 44, 229 and 241 (1918). The importance of the proper execution of each step in the treatment leading

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up to dyeing is strongly emphasized. This properly begins after the killing of the animal, when cuts in the hide should be avoided and putrefaction and thorough drying out prevented. Hides that are treated poorly in the beam house do not take up tannin uniformly and consequently dye unevenly. The hide must be softened completely before going into the limes and must receive neither too short nor too long a treatment. An insufficiently delimed hide will give rise to a clouded color and on the other hand a loss of hide substance can occur in the deliming process which will be noticeable on dyeing as an uneven color. The uppermost layer may often be partially destroyed and hence it will not give the polish and closeness of the healthy grain. The beginning of tanning frequently receives too little attention; the spots which may occur here, although they can be removed in the course of tanning, will result in a very uneven color on dyeing. The leather should be washed properly, previous to dyeing so as to remove excess tanning material and free acid. Oiling with drying or non-drying oils of animal, vegetable or mineral origin leads to different results. Light, pure, fish oil is the best for vegetable leather, but neutral emulsions of neatsfoot, cottonseed, castor oil and the like give good results. As the last step, drying should be carefully executed. The manner of dyeing and the correct choice of dyestuff is of especial importance, according to the manner of dyeing the difficulties are different. Certain dyestuffs are absorbed easier by the grain, others by the flesh and wounds in the grain. The leather should receive a thorough washing to remove all uncombined and superfluous tanning material and then be retanned in sumac so as to give a color that will be uniform and fast to rubbing. In the case of vegetable tanned leather that has been stored in the dry state, and subjected to the changes which are furthered by the influences of light, air, dust, gases, etc., surprisingly good results can be obtained by stripping by means of alkalies (borax, soda or soap) first and then retanning with sumac.

The basic dyes are products of extraordinarily high coloring power that require no other fixing material than the vegetable tannins, which is of importance for leather requiring long durability, such as leathers for book binding. Their colors are distinguished by great vividness and covering power, are usually fast to alkali and, in suitable combinations, are sufficiently fast to light. These dyes on account of their high covering power can be used for splits which have been coated with kaolin, green earth, etc. A very important group of basic dyes are the diamond phosphines which can be obtained in all current shades of yellow and brown and find their appropriate complements in the various brands—Manchester brown, Russian leather red, New blue, Brilliant green and Leather black.

Acid dyes, in general, require acid for fixing (sulfuric or formic) and when they are fixed with acid, they give colors that are completely fast. Leather can be colored through with acid dyes if it is free from acid. For light shades, that are difficult to equalize, it is customary to

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add the dyestuff with a slightly alkaline fat emulsion, or in the presence of soap. A combination worthy of recommendation, is the use of acid dyestuff as a bottom, topped with a basic dye. In this manner a color is obtained that is fast to light and rubbing and moreover permits the uniform coloring of grain damaged leather. The acid dyes which have proved especially good are the various brands of—Indian yellow, Fast brown, Havana brown, Brilliant crocein, Roccelin, Lana fuchsin, Cyanol, Fast blue, Napthol green, Formyl violet, Lanacyl violet and Napthol black, which alone or in suitable combinations suffice all demands.

The diamine or chrome leather dyes form an important group, and are already extensively used. They are completely absorbed by neutral chrome leather and give good colors that are fast to light and rubbing, moreover, they can be used in combination with acid dyes in the same bath, if it contains no acid, they require no mordant or fixative.

The usual methods of dyeing are:—tray or paddle, drum and brush dyeing. Spray dyeing is mentioned as a method that contains many possibilities for large scale operations upon perfection of a few present deficiencies.

Tray or paddle dyeing uses more dyestuff than the brushing method but a certain economy of time and labor can be obtained which in many cases determines the use of this process. It is easier to obtain a good even color by this method than by brushing, because the dyeing can be retarded.

Drum dyeing offers an economy in dyestuff, accelerates the penetration of the dye solution, drives the dye more into the interior of the leather and the dye is united better with it. But since leather is not homogeneous and differs in structure in its various parts whose resisting and absorptive capacities differ, the drum cannot be considered as the ideal dyeing machine.

The oldest and most widely distributed mode of dyeing is with the brush, it is operated either by hand or machine. Soft long hair brushes are, generally, only suitable for dyeing wet leather that absorbs the dye solution easily and uniformly. For firmly tanned or heavily oiled leather it is best to use a brush with short, stiff bristles. In order to obtain the best uniformity of color, the texture of the different parts of the leather must be considered, its firm and loose parts are brushed over correspondingly more or less strongly or often. Generally dry leather possesses a greater affinity for the dyestuff and therefore it is to be dampened before dyeing in order to obtain a more even color. If very light shades are to be dyed then the solution is to be diluted as much as possible, and with acid dyes, which are principally of importance for this purpose, a small addition of soap is made to it, or a weak solution is brushed on before the dye solution. The requisite addition of acid is best made with the second coating. G. W. S.

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PATENTS.

Enamelled or Patent Leather. British Patent 138,130. CORNELIUS HEYL, Worms, Germany. Jan. 24, 1920. In the process of manufacturing glazed, varnished, or japanned leather, artificially dried air is passed through the drying-stoves at a little above atmospheric pressure. Cooled brine from a refrigerating-machine is led through pipes to a system of radiator tubes installed in a chamber in front of the drying-stove in which the skins are suspended from racks. The air passing through the chamber is deprived of its moisture by cooling and, by means of a fan is caused to flow through a flue into the drying-stove, which contains heating-pipes and an outlet pipe.

Waterproofing Compositions. British Patent 138,185. J. H. TULLY, Mount Grove, Birkenhead. Feb. 26, 1919. A waterproofing and polishing composition for leather is made up of the following ingredients melted and mixed together in a glue pot: glue 1 oz., bees-wax 2 oz., rosin ⅛ oz., oak varnish 2½ oz., petroleum jelly ¼ oz., vinegar ½ oz., turpentine ½ oz., benzolene ¾ oz., and one table-spoonful of vegetable black powder.

Synthetic Tanning Agents. British Patent 138,796. A. G. BLOXAM, London. May 27, 1919. Formaldehyde condensation products are obtained by condensing formaldehyde (or substances yielding it) with mixtures of naphthylamine sulphonic acids and aromatic monohydroxy compounds containing acid salt-forming groups, at 60—80° C., in the presence of a little sulphuric acid. The resulting solutions may be used directly for tanning, after neutralizing by alkali the free sulphuric acid present. Products of increased tanning value are obtained by neutralizing the free sulphuric acid in the solutions by hydroxides of metals whose salts have tanning properties, e. g. chromium, aluminium, or iron, with or without neutralizing the sulpho groups by alkali. According to examples:—(1) β-naphthol is sulphonated and the product condensed with formaldehyde and 2 - naphthylamine - 6 : 8 - disulphonic acid, the resulting solution being neutralized with aluminium hydroxide and soda; (2) the mixed sulphonic acids of *m*- and *p*-cresol are condensed with formaldehyde and 2 - naphthylamine - 3 : 6 - disulphonic acid and the product neutralized with aluminium hydroxide; (3) β-naphthol is disulphonated and the product condensed with formaldehyde and 2 - naphthylamine - 3 : 6 - disulphonic acid, the solution being neutralized with chromium hydroxide and soda; (4) β-naphthol is sulphonated, the product condensed with formaldehyde and 2 - naphthylamine - 7 - sulphonic acid, and the solution neutralized with chromium hydroxide and soda; (5) β-naphthol is disulphonated, the product condensed with formaldehyde and 2 - naphthylamine - 7 - sulphonic acid, and the solution neutralized with ferric hydroxide.

Making Leather. British Patent 138,930. E. DURIO, Turin, Italy, Feb. 12, 1920. *Stretching by tension.*—In stretching tanned skins, an equal tension is applied over the whole surface by means of a number of

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independently movable gripping-elements comprising pivoted jaws connected by links to rods so that the grip of the jaws increases with the tension on the rods.

Leathers. British Patent 139,794. BALLONHULLEN GES., Tempelhof, Berlin. March 3, 1920. A substitute for goldbeaters skin, for use as a balloon envelope material, is prepared from the entrails of horses, cattle, pigs or sheep, or the stomach skin of the ox. The entrails are dissected, treated for the removal of impurities, fat, etc., then treated with oils or fats or emulsions thereof and with agglutinants. To prevent the material from becoming brittle, it may be treated with glycerine. The pieces are stuck together in one or more layers by means of an adhesive. The material may be used in combination with goldbeater's skin or with a suitable fabric, adhesion being obtained by means of an agglutinant and rolling. The finished article is waterproofed by varnishing.

Leather-Skiving Machine. U. S. Patent 1,336,597. GEORGE ORVILL TERRY, Minneapolis, Minn. Filed Aug. 25, 1919.

Leather Substitute. U. S. Patent 1,336,858. JOHN D. PRINCE, Boston, Mass. Filed Dec. 7, 1918. A composition of matter useful as a leather substitute, comprising rubber and wax of the Montan class, whereby the said composition of matter has the tough, slow-flexing qualities of leather and is devoid of the springy, elastic qualities of rubber.

Artificial Leather. U. S. Patent 1,337,802. ALBERT A. SOMERVILLE, Flushing, N. Y. Filed Jan. 15, 1918. A process of the kind described, which comprises winding into a roll a vulcanizable rubber layer and sheet of paper in intimate surface contact with one another, subjecting said roll to the action of a vulcanizing medium, and removing said paper sheet, thereby providing a material having the appearance, texture, flexibility, and in general the characteristics of dull finished leather.

Machine for Stretching Hides. U. S. Patent 1,338,050. FRANK W. TUCKER, Lynn, Mass. Filed July 25, 1918.

Dressing for Leather and Leather Substitutes and Process of Making the Same. U. S. Patent 1,338,286. ALFRED R. CALDWELL, Pasadena, Cal. Filed Aug. 4, 1919. A quickly drying liquid dressing for leather and the like consisting of the following ingredients in the proportions stated: asphaltum—1 gallon, benzin—1 gallon, rubber cement—1 quart, black pigment—1 pound, Japan drier—1 pint, and beeswax—¼ pound.

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CONTENTS

Elections - - - - - - - - - 449
Correction - - - - - - - - 450
Council Meetings - - - - - - - - 450
The True Tanning Value of Vegetable Tanning Materials. Discussion. 451
The Sampling and Preparation of Sole and Harness Leather for Analysis Preliminary Committee Report. By F. H. Small, Chairman - 475
Unhairing of Hides and Skins by Enzyme Action. By Chas. S. Hollander 477
The Time Factor in the Adsorption of Chromic Sulfate by Hide Substance. By Arthur W. Thomas and Margaret W. Kelly - - 487
The Determination of Total Saponifiable Matter in Sulfated Oils by Difference. By Ralph Hart - - - - - 495
Abstracts - - - - - - - - 499

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Percy Ingham Neeld, 1330 Oak Lane Ave., Oak Lane, Philadelphia, Pa.
Percy Simpson Butler, Box 226, Kingsport, Tenn.
Roy Sanford Kratz, 4909 N. 12th St., Philadelphia, Pa.

CORRECTION.

Page 326 equation (1), $\log [H^+] = a + b\,m$. Should read $\log [H^+] = \log a + b\,m$.

COUNCIL MEETINGS.

At the close of the executive session of the A. L. C. A. at Atlantic City on May 29, 1920, the new council was convened. Upon the resignation of F. H. Small as ordinary member of the council to accept the presidency, G. W. Schultz was elected to fill the vacancy. The business of the meeting consisted principally of considering applications for membership.

The second meeting of the Council was held at the Chemists' Club, New York City on June 14th. J. B. Churchill's resignation from the council was presented and accepted and C. C. Smoot III was elected to take his place.

The committees formed for the present year were as follows:

Sampling and Preparation of Leather for Analysis.
F. H. Small, Chairman.
Determination of Moisture Content of Leather.
R. Wright, Chairman.
Determination of Water Soluble in Leather.
J. A. Wilson, Chairman.
Determination of Epsom Salts in Leather.
R. W. Frey, Chairman.
Determination of Oils and Fats in Leather.
F. P. Veitch, Chairman.
Determination of Glucose in Leather.
J. S. Rogers, Chairman.
Measurement of the Plumping Powers of Tan Liquors.
A. A. Claflin, Chairman.
Color Measurement of Vegetable Tanning Solutions.
Dr. T. Blackadder, Chairman.
Dr. Thomas' Method for the Determination of Sulphuric Acid in Leather.
Dr. A. W. Thomas, Chairman.
Alternative Filter Paper.
H. C. Reed, Chairman.

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The council requested the chairman of the committee on Sulphonated Oil Analysis to have the recommendations of this committee republished together with the discussion on the subject at the annual meeting, at the same time requesting criticisms and recommendations from the members so that the proposed method can be corrected and presented for adoption.

The committee on the Complete Analysis of Chrome Leather was requested to consider a few minor changes in the method proposed before it was presented for adoption.

In consideration of the suggestion of the S. L. T. C. that we co-operate in our committee work, the suggestion was very favorably received and the secretary was advised to notify the secretary of the S. L. T. C. to this effect and to propose a scheme for consummating it.

THE TRUE TANNING VALUE OF VEGETABLE TANNING MATERIALS.

Discussion on the paper by J. A. Wilson and E. J. Kern[1] after its presentation at the annual meeting of the A. L. C. A. at Atlantic City, May 27, 1920.

J. A. WILSON: The question has arisen as to whether or not the new method represents tannery conditions. Some of the sole leather men have told me that it does not, and of course that is a very vital point; if you are going to use a method in investigational work in the tannery, it must satisfy the conditions of the tannery.

We have a cost system covering our yards that has been running for a number of years, and as a demonstration of the value of the new method, at least in our type of work, I have taken one of the yards for a period of three years, which I think is quite long enough to give a pretty good average of conditions. We know all the hide substance which entered that yard over the three-year period; we have all the tanning materials, and their analyses by the official method, right to the pound, that entered that yard during the same period. We have complete analyses of the leather, sampled properly from certain lots as they came through (and we destroy a whole skin every time we make a leather analysis so that there is no difficulty due to getting parts

[1] This JOUR., 15, 295 (1920).

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of the skin or hide that are not representative), and we find that if the official method is correct, we are losing half the tanning material we put into the yard; to be exact we got out in the form of finished leather 50.6 per cent. of the tannin that was put into the yard.

We are not bothered much by fermentation, such as apparently takes place in the sole leather yards; there is very little precipitation; and we have almost no sludge, so there could hardly be a great deal of wastage of actual tannin.

It is regrettable that we haven't analyses by the new method over the same period, but we can at least analyze the same mixtures to-day that we have been using over this period and assume that there has been a reasonable constancy in those materials, and we get just 52.3 per cent. as much tannin as is obtained by the official method, which is not very far off from our 50.6. I think that 3 per cent. of the total tannin put into the yard would represent a reasonable wastage, and I am certain that 50 per cent. would not.

I know nothing at all of the condition of the sole leather yards, although I believe Mr. Yocum some two or three years ago presented a report in which he said there was a great loss of tannin in a heavy leather yard, which was never accounted for; it was lost in some mysterious way, but I don't think any satisfactory explanation was ever given.

Now I think we have that explanation, because the errors he mentioned in his work are of about the same magnitude as we find for hemlock liquor, and I hope that in the discussion the viewpoint of the sole leather people will be brought out, because we haven't any access to figures of that sort.

There is a great deal more to be done on this work. The method in its present form is barely a few months old and we have not yet been able to follow out every line that has occurred to us, but I should be very glad if we could get the opinion of men working especially in lines different from our own.

R. W. GRIFFITH: One or two things impressed me, as I listened to Mr. Wilson, which I would like to bring out. The proposed method does not seem to me to be any more scientific than the present official method, inasmuch as it is not a direct

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method for the determination of tannin, so-called. Mr. Wilson arrives at his results by difference, just as we do by the official method, excepting that we take liquors and he takes the tanned hide powder. There is another thing which I thought of, in connection with Mr. Wilson's talk, which has to be taken into consideration when we try to approximate a laboratory method to tan-yard conditions, and that is the time factor. If you tan leather in a practical way with any given tanning materials, by a quick process, and proceed then to tan with those same materials by a slow process, you get two very different leathers; the only difference in the manipulation being the time factor. I don't know just how Mr. Wilson can reconcile his method to include the time factor which operates in the process of tanning.

Mr. Wilson, himself, has anticipated a good many of the objections, or the criticisms to his method, especially with regard to it being a practical method for every-day work. There is no doubt but that Mr. Wilson's work is extremely valuable. His findings at least indicate what you might call the absolute, fixed matter obtained from any given tanning material.

DR. LEVI: Mr. President, in confirmation of one of Mr. Wilson's statements, if I remember correctly, it was about 1895 or 1897, when gambier went up from about 3½ to 8½ cents; gambier was then almost prohibitive to the sheep-skin tanner, and in order to get a substitute for gambier, we used quebracho with a mixture of nutgalls, and also gambier with a mixture of sumac, and found out that we got a leather very similar to the gambier tannage. Of course, at that time I wasn't far enough along in the tanning industry to really think, or know, that I had some gallic acid there; but Mr. Wilson's statement this morning brought back to me that old experiment which was made in 1895 to 1897.

G. W. SCHULTZ: The determination proposed by Mr. Wilson, rests or falls on the assumption that the compound collagen-tannin is a definite chemical compound; and also that this compound is stable and insoluble in water. According to all information that is available on the subject, as far as I have been able to ascertain, this is not generally recognized, in fact,

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the assumption has been directly to the contrary. Procter is on record as saying, in his work on gelatin-tannin compounds, that the compound can be washed indefinitely and still tannin can be removed; and J. T. Wood, on the subject, states that water decomposes the compound, and furthermore concludes that the compound is an adsorption compound; that its composition is not constant, but depends upon the concentration and relative proportions of both substances.

With reference to gallic acid and the assumption that all non-tannins act in the same manner, as far as adsorption by hide powder is concerned, it may be justified, and may not. The only non-tannin of this character, that has received attention in that respect is gallic acid, which Mr. Wilson referred to in his paper on the subject several years ago. At the most we can say that only acid substances act in the same manner as gallic acid; they combine with hide more or less, and give what we might call a false tannin value; give too high a value for tannin. A normal chestnut extract will give a maximum content of acid by our method of about 2 per cent., calculated as acetic acid, granting 50 per cent. for absorption in the precipitation of tannin this would give a maximum of about 4 per cent., or the equivalent of 12 per cent. gallic. Allowing for a 50 per cent. absorption in the tannin analysis this would make a tannin error of 32 per cent. in excess of the true tannin content providing that all of the acid found were gallic.

Perhaps the sole leather chemist would be inclined to ask what becomes of all the tannin that is found in the liquors at the present time. We start out with a given amount and we end with a given amount, and it is a daily occurrence to analyze sap liquors that contain one-tenth to two-tenths per cent. tannin by our method, and these liquors will still tan hide; we can tan skivers with them and make leather, and it isn't at all uncommon to have liquors that contain practically no tannin.

There is another point that Mr. Wilson referred to which concerns astringency, that I am not inclined to agree with altogether. It has been generally recognized by leather chemists that astringency follows the order, somewhat, of the ratio of tannin to non-tannin; in fact, we can go further and say that practical tan-

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ners have recognized the same thing; but there is also another factor which reduces astringency and that is dilution. We can take a very astringent liquor and make it sufficiently non-astringent to tan with properly by simply diluting. Furthermore, when bisulphiting quebracho extract, we only increase the non-tannin slightly; in some cases we increase the purity, and this tanning tannins than chestnut extract would have, and still the hemlock material will be less astringent than ordinary quebracho; in fact, it will be very mild and will penetrate rapidly. And there are instances of hemlock liquors, with a higher percentage of non- would have a higher astringency.

The recent work that has been done on the so-called colloidal tanning solutions by Cross, Greenwood and Lamb, and the patent recently obtained by Carmichael, based on adding starch to strong liquors and thereby decreasing the astringency, would point to another factor that would have an influence.

We have done a little work on the method suggested by Mr. Wilson, but I don't feel inclined to give the results at the present time because the work has not been sufficient; we have only had a small amount of time at our disposal, but I will say that the results we obtained were entirely different from Mr. Wilson's. Furthermore, we have taken the non-tannins and washings and reconcentrated them under a high vacuum to the original volume of 200 cc., and have tanned hide powder with it, and, by the calculations employed, we have found a definite percentage of tannin, which would account for some of the difference that Mr. Wilson finds, but perhaps not all of it.

R. W. GRIFFITH: One of the most valuable features that we always supposed attached to our official method was the fact that it would give us very good control of yard work. I was rather surprised to hear Mr. Wilson say that in his operations it gave absolutely no control at all; but as the proposed method did give very good control, you might tell us, Mr. Wilson, what yard you have referred to.

MR. WILSON: I was not speaking of routine control of liquors. In investigational work on new methods we have never been able to account for all the materials used, on the basis

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of the official method, by analysis of the leather, and usually would be short by an enormous amount.

If you have a yard running perfectly smoothly, there seems to be some approximate ratio at least between the new method and the official method, so that you could actually get a certain control with the official method just as you could with the new method; but I think you will find that you go very far astray when you begin to do real investigational work, not control work.

While I am up, I might refer to some of the question that have been raised. As regards the time factor, I don't think the new method is concerned with the fact that you get different results when you tan more quickly. If you tan more quickly in the yard, with a strong liquor, you find that you actually get a great deal more tannin carried away in the leather, and of course you get different properties.

In regard to the point which Mr. Schultz has raised on the matter of definite proportions, if we are dealing with a purely chemical compound in leather, it doesn't necessarily follow that tanning under different conditions we will always get the same amount of tannin fixed per unit of hide substance. You all know of the work that we have been doing on chrome leathers, in which we made very wild speculations, you might say, regarding the equivalent weight of hide substance as being 750, but we actually got results with chrome leathers which seem to bear that out; that is to say, that under certain conditions, using stronger and stronger liquors, we got what might be called a dichrome leather, and under other conditions we got what might be called a tetrachrome leather. Obviously, leathers which are mixtures of the dichrome and tetrachrome compounds can have any ratio of chrome to hide substance from that of the dichrome to that of the tetrachrome leather. With vegetable leathers I have taken Fischer's pentadigalloyl glucose as a basis. If we take a fifth of its molecular weight as representing its equivalent weight and use our value 750 for collagen, we can calculate the minimum amount of tannin, provided it were uniformly distributed throughout a hide, that would make leather. The calculated value, 45.3 grams of tannin per 100 grams of hide sub-

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stance, is very close to the low point that we find in vegetable leathers. If we have a uniform distribution of the tannin and have hit that figure, or one greater, the leather passes. If it is slightly under, it is always slightly undertanned. Our findings seem to bear out that figure very closely.

Without using any great excess of tannin; that is to say, using rather dilute liquors but increasing their strength, we seem to approach a figure which is just double that. Of course, you get different proportions of tannin to hide substance, but what you have are different proportions of the mono-tannate to the di-tannate.

In regard to *adsorption,* we are dealing with a much disputed term. You hear arguments as to whether adsorption is a chemical action or not. If you accept Langmuir's work, adsorption is purely chemical and there is no argument involved. I feel certain that so-called adsorption compounds of hide and chrome and of hide and tannin are actually chemical compounds.

As for the literature which Mr. Schultz mentions, I am perfectly familiar with that work, and I believe that Procter and Wood would uphold me in my statements.

In regard to non-tans, I might refer to the work of Procter and Blockey, in which they used a good many non-tans, and found that adding these non-tans to a tan liquor always raised the per cent. of tannin.

We experimented with gallic acid because it was a very simple thing to deal with; it was comparatively a strong acid, and we could get big effects. We purposely tried to get big effects just to show that those conditions did obtain in tan liquors.

Of course, when we refer offhand to a large proportion of non-tannin to tannin, we really mean a large proportion of those non-tannins which form compounds with hide. I believe all the hydroxy-benzenes and their acids combine in that way. But if you should add glucose, which certainly would be considered a non-tannin, I don't think you would have any great effect upon the astringency of the tanning material.

As for the sulfiting of a quebracho extract, it isn't simply a matter of adding non-tan in that case. If you put a sulfate or sulfite radical into your tannin, you might expect very different

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properties. You know that is true when you deal with cellulose, and why shouldn't you alter the properties of the tannins? We don't claim that the lack of non-tans is solely responsible for astringency. Tanning materials undoubtedly do differ in a great many respects. We have two different classes of tannins and couldn't very well say that both classes represent only one kind of tannin. They are probably very different. The reds of quebracho are certainly very different from the tannin of some other materials.

Of course, I am not prepared now to deal with the last point which Mr. Schultz brought up about concentrating the wash liquors; the method is still new, but that is a point which we can well afford to take up, and we are going to follow some of the results that he has obtained, with a great many different tanning materials, and we shall be glad to report the findings as soon as they are available.

H. C. REED: I would like to ask Mr. Wilson whether he was correct in his statement to the effect that the addition of non-tannin matters to the tanning solution always increased the tannin, as shown by the official method of analysis. I think he is incorrect in that statement, because in certain instances I can very well recollect figures to show that it decreased the tannin.

MR. WILSON: That is a thing that we have emphasized very strongly; if you add any material which doesn't combine with the hide, you will always decrease the tannin as found by the official method. I am apt to take it for granted, when I speak of non-tans in that way, that I mean those benzene acids. Two years age we showed that if you add salt to a tan liquor, the apparent tannin content will go down and that if you analyze a solution of sodium chloride without any tan, you will get a figure something like 104 or 105 per cent. for non-tannin or a negative value for tannin.

J. H. YOCUM: I have read Mr. Wilson's article in a rather cursory way, and want to tell you what my experience has been. I cannot give you data that would be publishable, as Mr. Wilson has, for the reason that it is the result of work which I have

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done and have been paid for; but I have found in my experience, that from 90-93 per cent. of the tannin, as determined by our present method of analysis, will be found in the leather, also following our present methods of analysis. This strikes me as being quite efficient. While Mr. Wilson's ideas may be new to us, Von Schroeder in 1891 presented the same thing that I am presenting. If Mr. Wilson had looked back into the history of tannin analysis, he would not have fallen into this unhappy position. The facts are that it has all been gone over, and it is hopelessly impossible to change over night, nearly thirty years of experience.

F. H. SMALL: Mr. President, there is a point in connection with this that is not altogether clear to me. My understanding was the same as Mr. Schultz's: that the method must stand on the assumption that there is a perfectly definite compound of tannin with hide powder, and only one. Yet I understand Mr. Wilson to say a few moments ago, that the combination of tannin with hide may take place in a number of different proportions, depending upon the exact conditions that obtain when the combination takes place.

Now, if I understood him aright, I fail to see that he is determining a definite quantity by his method, and if not, it would seem as though the results he obtains must be variable and dependent upon the conditions under which he brings the hide powder and the tannin into contact.

MR. WILSON: I see no serious difficulty there. We have determined the limiting case for the smallest amount of tannin that will combine with hide to make leather. Now, where you are dealing with polyvalent salts, you find that when the greater portion of any one radical has become fixed to the main group, that you have a sharp change; that is to say, that the second group does not attach itself as firmly. For example, if you have a substance like phosphoric acid, you know that the first hydrogen is readily ionized; there is a very big difference in the rate with which the second hydrogen is given off, and in ordinary solutions of the substance there is probably almost an infinitesimal amount of the third hydrogen given off.

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Now I think that we have actually a very sharp line for the first molecule of tannin which will combine. If you take calfskin and tan it in stronger and stronger liquors, you seem to approach a nearly limiting value. If you increase the concentration of tannin, the amount fixed seems to approach this first limiting value. Now there is a sharp change, and it takes much larger amounts of tannin to cause the same increase in the amount of tannin fixed, after you have passed that first point; and in our work the second limiting value seems to be an exact multiple of that first figure. If those things didn't go in exact multiples, we wouldn't have anything to base an argument on; but they do; one limiting point will be exactly double the other.

On the question of having hide powder in excess, if you have a definite chemical compound formed, it doesn't follow at all that you would therefore remove all of the tannin, because all these chemical reactions are reversible ones; or if they are not, they never proceed to absolute completion—there are always some of the reacting substances left. So you would expect, even though the amount might be extremely small, that there would always be some free tannin left in solution. We say you have completely detannized merely because you have lowered the tannin content to such a point that it will not make any appreciable difference in the results.

A. A. CLAFLIN: There is one point in regard to the nature of tannic acid itself, or what we call tannic acid, which introduces a complication which modifies conditions and should be recognized.

I believe absolutely with Mr. Wilson, that you get a definite chemical compound; that is, a combination of tannic acid with hide substance; a neutralization of electric charges; in other words, a chemical compound, but tannic acid is a weak acid of hydrolytic character, and experiments on the simpler forms of those acids show they have a tendency to combine with themselves; in other words, to go into the lactone formation, as it is called, or string themselves together, so that under certain conditions one combination includes, you might say, three molecules of the acid, or only one; that is, in strong tan liquors you have the formation of the lactones or anhydrides, which grad-

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ually disappear as you dilute the solution, and according to the dilution of the solution, you would get the greater absorption of these tanning materials. If you tan your hide powder, for example, in a concentrated solution, the presumption would be that the combination of three molecules of tannic acid would act simply as one molecule of tannic acid and combine with hide substance. Then, when you began to wash that, you would break up that three-string molecule combination and re-form tannic acid again. Now, if there is an excess of hide substance there, that tannic acid reformed, would combine with it. If there is not an excess of hide substance; for example, we will say all the simpler bonds of the hide substance are combined with molecules of tannic acid, then that newly formed tannic acid which heretofore has been combined with the other molecules of tannic acid will disappear in the wash water; and I think that that will give varying conditions, according to the dilution.

It will also explain the condition where sometimes you will get the formation of precipitates. It would also probably explain why you would get a greater absorption by using an acid in the liquors.

C. R. OBERFELL: It seems to me that Wilson's method stands or falls on the gelatin-salt test for tannin. Both Wood and Bennett, at different times, have shown that the tannin gelatin compound, or reaction, is reversible, which fact Wilson just referred to. Bennett states that the tanned hide can be completely detannized by washing. Now it strikes me that as this reaction is reversible, that in the washing of the tannin-gelatin compound, it may break up, or the tannin molecule may break up or decompose, and throw into the wash water compounds that are not precipitated by the gelatin salt reagent. Such a condition would readily explain the discrepancy in the Wilson method when compared with our present official method.

PRESIDENT GRIFFITH: Another point in connection with the washing of the hide powder, it depends upon the time of soaking of the hide powder. If you take well tanned leather and soak it for a long time, the tannin is reasonably combined with the hide, but it can be washed out with long soaking. There is a very interesting illustration of that fact published in the JOURNAL of

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May, 1919, by Mr. Churchill, who received a sample of leather that was obtained from the cargo of a steamer that had been wrecked in Lake Huron in 1865. The leather had been in the water from that time until 1918, and Mr. Churchill analyzed that leather and found that it was gradually returning to pure hide substance. The analysis on the absolutely dry leather showed a hide substance of 83.12; the load was 18.88, and the combined tannin was 13.11.

That would illustrate the fact that long soaking has a tendency to release the tannin which was originally combined.

MR. WILSON: If the reaction is reversible, there is no doubt, if you washed for an infinite length of time, that you would remove all the tannin. But in dealing with any chemical reactions you are concerned with how nearly complete are the reactions for the conditions under which you work. We found, after washing hide powder tanned with larch bark extract apparently free from all its soluble non-tans and analyzing it and then washing some of this same material a great many times more, that there was nothing further given up that could be detected by an analysis of the powder. That would seem to settle the question raised by Mr. Oberfell; although you may have a reduction due to the washing, it must be an extremely slow one, and we feel pretty certain from the work, as it has gone along so far, that it hasn't any effect upon the method.

H. H. HURT: I would like to ask one question: Did you ever determine the nitrogen in the wash water?

MR. WILSON: No.

MR. YOCUM: In years gone by, I have analyzed or have had analyzed, the materials that were put into the tannery and the leather coming out. I am not just at the moment able to give exact data, but I have found that under analyses by our present methods, we got into the leather 92 per cent. of the tannin that we put into the liquors. Now if we use Mr. Wilson's method, we can get only 51 per cent. of the tannin that is put in the liquors, which does not account for the amount of tannin that is actually in the leather.

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T. A. FAUST: I can bear out Mr. Yocum in one set of figures. I remember rather distinctly that in a heavy leather tannery we were able to account for all excepting 7 or 8 per cent. of the tan. This particular tanner had a leach house, and we had to make the allowance for the spent, and of course also for the runaway liquors.

There is only this one objection to the statement, which Mr. Wilson may bring up, and that is the fact that the analysis of the leather was made by the official method, which he claims is erroneous. I cannot see how there can be any such tremendous error in sole leather as he claims, and I don't think that he should disregard the time factor as quickly as he does, because I think it enters into this matter very strongly.

Mr. Wilson's contention last year was that leather formation was electrical neutralization, I believe. Well, most chemists claim that it is an adsorption—a word that he does not like—a physical adsorption, I mean to say. He has made several statements this morning in which he speaks of an actual chemical precipitation. My understanding is that the only chemical precipitation in leather formation is the precipitation between the quinones and quinone-like bodies and gelatin, and that the greater part of bark tanning is a physical adsorption, more or less reversible. Furthermore, that this physical adsorption is a slow adsorption.

Now if he goes ahead with his method and treats his hide powder with the tan solution, this physical adsorption has taken place, and if he treats it with a great number of wash waters; I believe he has taken tan out of the hide powder which in the tannery goes into the leather and stays there.

As regards upper leather, I will state that I believe the reason most upper leather tanners cannot account for the tannin is because their liquors are so near neutral, have so little acid in them, that they are not getting their tannin.

I would like to ask Mr. Wilson whether he has compared the method with the Lowenthal method. We don't accept that method as being particularly accurate, but I would like to know what comparison there is.

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I would also like to ask him, when he found only 50 per cent. of the total tannin in the upper leather yard, how did he analyze his leather—by the new or old method?

MR. WILSON: I will answer your last question first. The official method hardly comes into play in our work, because the leather contains only about 3 per cent. of water soluble matter. In sole leather undoubtedly you have a great deal of uncombined tannin in the soluble matter.

Now as regards the time factor, which Mr. Faust brought up, I would like to ask him how he accounts for the fact that if you shake hide powder in a tan liquor for six hours or forty-eight hours, you get exactly the same results with the new method. It doesn't make any difference whether the hide powder is in contact with the liquor for six hours or forty-eight hours, in our experience—we checked the results.

MR. FAUST: Will you explain to me why you get a great deal more combined tannin in long time tanned sole leather, than you do in a quick tannage?

W. K. ALSOP: And it also is tanned with less tannin; that is, the analyses show that there is not any more tannin thrown away in one method than in the other and less tannin is required for the long time tannage.

MR. WILSON: You have conditions there with the strength of liquors that I really don't think comes into play in this work. I would want some facts stated pretty clearly before I would pass an opinion.

MR. FAUST: I think you admitted that you haven't had experience with sole leather. We are bringing up these points because we all want the best possible method we can get. For instance, you brought up the matter of the different concentration of the tan solution as having a bearing on it. Now your error is greater than any one of the chemists here, who have had practical experience in tanning leather, will admit possible, so that there cannot be that much error, and I rather think that it is due, possibly, to the time factor. The time factor has some relation to it, as far as heavy leather is concerned, and possibly concentration also.

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H. C. REED: I haven't the figures with me—they were incomplete and I did not bring them—but I don't agree with Mr. Wilson's statement that by increasing the time, you will not increase the absorption, because I have figures that proved quite contrary.

MR. WILSON: We have figures on that, which we have carried out, ranging from 6 to 48 hours and which show the opposite of Mr. Reed's statement; so that seems to be more a matter of laboratory manipulation. Therefore, it is hardly open to argument at the present time.

C. C. SMOOT: We account for better than 90 per cent. of the material in our yards by using the present official method, and have for years.

MR. ALSOP: According to results shown, a tannery liquor showing 6 per cent. tannin by our method may show only 3 per cent. by the one under discussion. Consequently the non-tannins will be 3 per cent. greater by the latter. If this liquor is run down through the tannery in the tanning process it may show only 0.3 per cent. tannin by our method. If the extra 3 per cent. non-tannins shown by Mr. Wilson's method are not combined, or at least taken out by the hides, should they not show in the analysis of the runaway liquor?

MR. WILSON: When a hide is put into a liquor, it takes up non-tans as well as the tans, and if that leather is never washed, undoubtedly you will have them all there; and in that case, the yield ought to agree with the official method. If the leather is never going to be washed and you assume that everything you are going to add to the hide is tannin, I don't doubt it will agree with the official method, but I don't think it will agree if the leather is going to be washed.

J. M. SELTZER: I find, in analyzing the tannery liquors, that the non-tannins found in the fresh liquors will be found in the spent liquors that are sent to the sewer; but will be decreased somewhat by perhaps 15 per cent. In analyzing the fresh liquors we find a certain amount of tannin and non-tannins before the hides are placed in that liquor, but after the hides have been in

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that liquor for the required period, we will find about the same amount of non-tannins but a considerable reduction in the tannin which is in the amount of tannin which the hides have taken up. In neither case do the non-tannins change but very slightly except when taking a very strong liquor and running it down to a very weak liquor, when as in one yard 4.50 per cent. non-tannins enter the tannery and 3.86 per cent. non-tannins leave in the tan liquors to the sewer. The solid matter that is present in the fresh liquors in the tannery is run down through the yard to the tail rockers and the amount of non-tannins that are found in the fresh liquors are found in the spent liquors that are sent to the sewer while the tannin present in the liquors has been almost entirely removed by the hides which shows that the tannin removed by the hide powder in the analysis is removed by the hides in the tannery.

In the case cited by Mr. Wilson where he speaks about the acid causing the hide powder to absorb the tannin to a greater extent, that acid is present in the tan yards when the hides are tanned; that acid forms there and goes down through the process, and creates a higher absorption of tannin in the process than it would in the analysis by Mr. Wilson's method.

PRESIDENT GRIFFITH: Mr. Seltzer, with regard to the efficiency of the official method in connection with control work, what do you find the accuracy to be? Do you attempt to find pretty close control work by using the present method of analysis?

MR. SELTZER: By either method of analysis, the results would be comparative. If you can duplicate those results from one time to another, you can produce a comparison.

A. C. ORTHMAN: We have a sole leather yard and we keep cost accounting. We find, by analysis of our liquors, that we agree with our office on the amount of material used. There is one thing we do not find, and that is how much tannin is consumed in the yard by the analysis of the leather. That would probably explain why Mr. Yocum gets 92 per cent. efficiency.

MR. YOCUM: You don't deny, then, that you get 90 per cent. out of your liquors?

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MR. ORTHMANN: No, I do not, Mr. Yocum: we get 92 per cent. of the tannin used—possibly more; I have no definite figures for that. We probably get more than that. The efficiency may be better, or may be a little bit less, but I tried to explain that we do not analyze our leathers to keep tab of the amount of tannin consumed in the yard. We do not check our weight that way. We deduct those figures from the amount of tanning material used and the inventory of our yards by analysis of our liquors, not checking it by the analysis of the amount of tannin found in the leather.

MR. REED: Mr. Wilson, did you check up your figures for the last three years solely from the standpoint of non-tans from the original analysis of non-tans present and from the non-tans that went out and the non-tans of the leather?

MR. WILSON: We have checked it up from the basis of tannin, the only basis on which we could check it.

MR. SCHULTZ: In trying to check sole yards from the basis of non-tannins, as Mr. Reed suggests; with the present official method there will be a loss of non-tannins that cannot be accounted for. If you are going to increase those non-tannins several hundred per cent., then there will be a still greater loss.

MR. ORTHMAN: Going over to the analytical end of the method, I am fully satisfied that Mr. Wilson has proven that the official method is not what it ought to be, for the determination of tannin.

We did considerable work in that line with our reagent 33, which has been published, but we haven't had time to follow it up; we had occasion at that time to make analyses by the present official method, along similar lines as those to which Mr. Wilson has referred, and we have found also that there are many substances that were not tannin, that were absorbed by hide powder; and I feel fully justified in saying that our present method is not what it ought to be.

MR. YOCUM: Do you mean to say that the thing that you don't call tannin doesn't combine with hide to make leather?

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MR. ORTHMANN: Not in all cases, I don't agree with that: that everything that combines with hide is not tannin. We have absolute proof of that.

MR. YOCUM: No; but does it make leather?

MR. FAUST: We all admit that the present official method is not absolutely accurate; we always have claimed that we are not hitting the true analysis as in any specific chemical compound, but we do think we are getting somewhere close, possibly with an error around 5 or 10 per cent. of the true tanning value of these different tanning materials.

Now I believe Mr. Wilson has opened up some new ideas here, but when it comes to upper leather, I can't understand this 50 per cent. loss which he is talking about; I can't see how he proved that. As far as sole leather is concerned, of course he hasn't been able to get figures on that, but sole leather doesn't show any such loss, and this will be borne out by every one familiar with the subject, who is here.

PRESIDENT GRIFFITH: Of course, when we speak of tannin, we use the term in a very general way. Our European friends, in reporting their analyses, use the words "Matter absorbed by hide," which is really what we measure and what we call tannin by our method of analysis. After all, it is the matter that is absorbed by hide that makes leather; and that is what we want to measure: we want the correct measurement of the matter that makes leather, because that is what the tanner wants to know, and our work must be supplemental to the work of the tanner.

MR. ORTHMANN: From a scientific standpoint, I do not believe Mr. Wilson's method is correct. I agree with what he said in his opening remarks; we have still to account for the coloring matter which we admit is present in all tannins, which are absorbed by the hide powder and reckoned as tannin.

MR. ALSOP: I would like to ask Mr. Wilson what the true tanning value of spruce extract is?

MR. WILSON: It runs about 13 per cent. on an extract which by the official method would show about 26 or 27 per cent.

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MR. FAUST: That is even higher than chestnut extract, then. It will give 13 per cent., and according to the figures given chestnut will give 10 or 11; in other words, spruce extract has more tannin in it than chestnut extract!

MR. WILSON: That, I think, is correct. In regard to the point that Mr. Faust brought up before, I would like to ask him if he has any figures on the fixed tannin in his leather, as compared with the amount of tannin that enters the yard?

MR. FAUST: The figures which Mr. Yocum referred to, gave the analyses of the leather, which shows the combined tannin and the uncombined tannin. We also have the analyses of everything that went into the leach house; also the tannin that was thrown away as spent, and the amount of tannin that was run away in the run-away liquor. In adding that up, we were about 7 or 8 per cent. short. But you can take this assumption: that the figures mean nothing because in all cases we analyzed by the official method.

MR. WILSON: What proportion of the total tannin appeared as fixed tannin in the leather.

MR. FAUST: We know the percentage of total tannin in all that leather and the number of pounds of leather in the yard.

MR. WILSON: I would be very glad to have the figures.

WM. H. TEAS: Mr. Chairman, I think possibly there is a disposition to confuse the chemical determination of true tannic acid with what the tanner buys to tan leather with. Now, whether the proper method of determining true tannic acid is by the method which Mr. Wilson proposes, I don't know. I question it, because it doesn't seem to me that it is a scientific method.

So far as our method is concerned, we all know that is isn't the best method, that we would like to have. We have known for twenty years the effect of gallic acid and oxalic acid, and similar organic acids, that accompanied many of the tanning materials, but notwithstanding their effect, so far we haven't been able to get another method which will approximate, in concordant results, the one we are using. Now, as I understand it, your

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method, on hemlock bark, for example, would show 6 per cent. tannin in the bark?

MR. WILSON: Yes, sir.

MR. TEAS: Then any practical tanner here would get only 120 pounds of tannin from a ton of hemlock bark without taking into account any of the tannin left in the spent tanning material by virtue of bad leaching. I don't believe there is any tanner who will admit that he didn't get more than 120 pounds of tanning material out of a ton of hemlock bark. I wouldn't say that you can account for 92 per cent., but I think it is a pretty safe statement to make, that any efficient tanner in the sole leather line will get from 85 to 90 per cent. of the materials he puts into the job.

MR. WILSON: I wonder if they really have figures to prove that? I don't think I would want to accept it without seeing some figures for the fixed tannin.

As regards this new method of determining tannin, I think we have taken care of that in the opening part of the paper, in which we mention that what it does determine is the material that forms a stable compound with hide substance, a compound that resists washing. That is all the method calls for. We make no claim that it determines pentadigalloyl glucose.

MR. TEAS: The tanners have their figures. Of course, they haven't figures running far back, so far as the chemical end is concerned. So far as the financial condition is concerned, they have their figures.

MR. WILSON: I would like to know how they got any more than that. They are including a great many things in that leather that they know are not tannins.

MR. TEAS: No, not in that; they have taken account of the oil that is put in, and the moisture, and where they put in glucose and salts, that is taken account of; but I will admit that they are calling tannic acid, stuff that comes out of oak and hemlock bark, and it will take the Almighty, to differentiate between them.

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MR. WILSON: Well, Mr. Teas, couldn't we have some of these figures made available? I think it would clear up the situation a great deal, if we had figures to go on.

PRESIDENT GRIFFITH: Mr. Wilson, it seems to me that there must be a limit to the approximation of your method (what is described as your method) with actual practice, for the reason that when you ask for actual figures from the tannery as to what they get, of course they get their results by direct weighing of the leather. You get your results not from leather but from a very finely divided powder, which is very susceptible to washing and consequently to the removal of a good deal of the matter which really makes leather, because when it is in leather it is in an entirely different physical condition than it is in combination with hide powder and I don't think you could expect to find a very close approximation between your method and actual practice, because you are not going to wash out leather, unless you grind it up, so that it approximates hide powder, which it is not intended to do in commercial use; and, after all, the last analysis of this is the commercial proposition in the production of actual leather. What you put into that, of course, is the material which you are trying to determine by your method. While your method has considerable merit and is valuable, it has very, very great limitations as to its practical application in the control of the production of leather.

MR. WILSON: But how do you account for the fact that we do find that it agrees with practice?

PRESIDENT GRIFFITH: So far as sole leather and heavy leather tanning are concerned, I haven't been able to find that your method is applicable. You are speaking of upper leather, a class of leather which I don't think we have very much information on, as far as tannery control of liquors is concerned.

MR. WILSON: But I don't find any figures available for heavy leather in such form as could be applied to this work.

PRESIDENT GRIFFITH: I think you will find that a great many tanners have those figures, which I don't think they are ready to have published.

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MR. WILSON: If they are not, of course we cannot very well be expected to accept the statements made on the subject.

J. M. SELTZER: Mr. President, the difference between the manufacture of upper leather and sole leather is quite marked. I should think that the manufacture of upper leather was somewhat similar to our method of analysis, inasmuch as it is a more rapid tannage. We have had some cases in our laboratory, for instance, with quebracho extract where one of the operators used one and one-half times the amount of extract that he should have used in making up the solution for analysis, and when we checked our results and found that too large a quantity of tannin—somewhat close to six-tenths of one gram of tannin per 100 cubic centimeters instead of four-tenth grams as called for under the official method—and when repeating the determination using the required amounts of the official method for analysis we found that the percentage of tannin was exactly the same in both analyses. The quebracho tannin is more astringent and is absorbed by the hide powder more quickly than the chestnut tannin and other tannins of the same nature. Chestnut extract would not act in a similar manner as the percentage of tannin found in a solution stronger than the official method would be very much lower than when the official amounts would be used which shows that the hide powder will absorb larger amounts of quebracho than it will chestnut extract when tanned in only one solution. This same thing would occur in the actual tannage in a tannery and is one of the causes why catechol tannins have higher weight giving properties in the manufacture of leather because the leather will absorb larger quantities of that form of tannin. This does not mean that the material not taken up by the hide is not tannin, but that the hide will absorb larger quantities of certain kinds of tannin than it will of others, but if the tannage is properly regulated the entire amount of tannin entering into the tannery can be placed into the hides at some point of the process.

In sole leather tannage the tanner runs a stronger liquor over the hides that are nearly tanned, and the tannin that is not absorbed runs down through the yard over the various layers, those tannins which are very weak proceed down through the yard until they come into the rockers, where the rockers receive the hides in a green state, that is, almost 100 per cent. hide substance, and

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those hides can absorb the tannins that are only slightly astringent and can take up those tannins and as the hides proceed through the tan yard, in a period of three months to one year according to the length of tannage they absorb the tannin in a slow manner allowing the more astringent tannins to be taken up by those hides in the last stage as the hides have become saturated. In making an analysis of the liquor and putting in the hide powder and shaking it for a given period, the hide powder will absorb the more astringent materials, and those tannins which are less astringent may probably not be absorbed and are washed out by Mr. Wilson's method of analysis. In the sole leather tannery all of the tannins are actually absorbed by the hides and the tannin gives the weight to the finished leather. In the upper leather tannery, I think, they may lose a large quantity of tannin which is sent to the sewer by the washing of that leather, but in the sole leather tannery that tannin is saved and enters into the hides by running the tannin liquors over various lots of hides in different stages of the process. The weaker liquors are always placed on the hide which is in the first stages of tannage so that the tannins more difficultly absorbed by more completely tanned leather will be easily absorbed by the green hide. This shows that the time factor must be considered in any analysis for the determination of tannin if it is desired to determine the percentage of tannin from the amount of tannin combined with hide substance, and it must be certain that all of the tannin in the solution for analysis is completely absorbed by the hide substance which removes the tannin from the solution which is being analyzed.

F. P. VEITCH: Mr. Chairman, I am wondering if the difference between the two methods isn't really greater than it appears to be. If I followed Mr. Wilson correctly, he works with the solution from which the reds are not removed. Any reds or insolubles not washed out subsequently would appear in the results as combined tannin, thus making the figures for tannin higher by the proposed procedure than they would be if the clarified solution were employed.

MR. SCHULTZ: The point that Mr. Veitch brought up is perhaps worthy of a little more discussion. Mr. Wilson does not

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clarify his solution before detannizing. The reds, or the insolubles will be fixed by the hide and calculated as tannin in the new method. Operating with quebracho extract, which has a very high per cent. of insolubles, it would increase the error considerably. Then the tannin as found by Mr. Wilson's method should be compared with the sum of the insolubles and tannin as found by our method.

MR. WILSON: That would make the difference even greater than it is; wouldn't it ?

MR. VEITCH: That is my idea, Mr. President, that the difference is probably greater than it appears from Mr. Wilson's results. In other words, if you are going to compare these two methods on the same basis, the reds of the present method must be added to the tannin and instead of having a 200 per cent. difference, there might be a 300 per cent. difference.

G. L. TERRASSE: I would like to inquire, Mr. Wilson, whether any nitrogen determination was made on the wash waters of hide powder?

MR. WILSON: No, we did not make any such determinations.

MR. TERRASSE: Is it not possible that in some of the weaker solutions rather large nitrogen losses took place?

MR. WILSON: I doubt it. We did not carry out that phase of the work as we did not think it pertinent to the question, but it can easily be tested.

MR. VEITCH: Mr. Chairman, I would like to have that point made a bit clearer. Do you refer to the washings from the hide powder or the washings from the tanned hide? I don't see what difference the solution of some hide powder would make. If any of the hide powder goes into the solution, you don't have that portion when the remainder is tanned; it's gone.

MR. TERRASSE: I refer to the washing of the tanned hide powder.

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MR. VEITCH: I think that any nitrogen that may have been washed out of the untanned hide has nothing to do with this question, whatever. However, if any nitrogen is dissolved from the tanned hide, that is another proposition. I would just like to repeat in this connection, Mr. President, what I have often said before these meetings; that in our experience a tanned piece of hide can be washed for a long, long while without any evidence of disintegration whatever. I agree with Mr. Wilson, that there is very little danger of the decomposition of the leather. I believe you will come finally to a place where the leather slowly decomposes, but it is so far beyond the point to which he has gone, that I am not at all bothered with that feature of the method.

MR. SELTZER: Is there no loss in a mechanical way in the washing of that hide powder?

MR. WILSON: It wouldn't make any difference if there were. You are only determining the ratio of tannin to hide substance; you don't care whether you lose any of the hide powder or not, so long as you have enough left to make an analysis.

THE SAMPLING AND PREPARATION OF SOLE AND HARNESS LEATHER FOR ANALYSIS—PRELIMINARY COMMITTEE REPORT.*

By F. H. Small, Chairman.

I feel fully convinced that tanners and others interested in leather analysis are a long way from appreciating the importance of sampling. The great majority still think that if they give you a piece of leather taken from a hide, no matter from what part, an analysis of this sample will be equally an analysis of the whole leather from which the sample was taken. The effective way to correct this opinion would seem to be to submit analyses showing the varying composition of a whole hide over its entire area. If it is shown that leather from one part of a hide contains say 5 per cent. more soluble solids than from another part; that in the same butt one sample contains 3, or 4, or 6 per cent. more hide substance than another; that one sample contains twice as much salts or sugar, or what-not, as another, and then

* Delivered at the Annual Meeting of the A. L. C. A. at Atlantic City, May 28, 1920.

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these facts are laid out before them in the form of a picture, it seems probable that it will impress upon them the necessity of securing an accurate sample.

In the work that has been done on sampling, so far as I have been able to discover, there has been no way of telling absolutely whether the method of sampling that was used, or was proposed, was accurate, in other words, no figures representing the average analysis of the whole hide have been available.

Those of us who are working with heavy leather are not so fortunate as Mr. Wilson, in being able to take our samples by using a whole hide for the sample. Yet it does seem absolutely necessary that we should have analyses of whole hides before we can determine whether a particular method of analysis is adequate or otherwise.

The Committee, therefore, has had in mind using the whole half of a hide, dividing that up into sections, the sections being, as well as they can be selected, of essentially the same composition, the size of the pieces, therefore, probably being more or less variable; each piece being prepared for analysis in its entirety, and an aliquot sample taken and analyzed;—these divisions of the hide moreover being taken so that they will give us by putting together a certain number of them, the ordinary commercial cuttings; in other words, a certain number of them put together will give us a bend, another number put together will give us a belly, another number put together will give us a shoulder, a head, etc; and in that way we can build up a side, or a half hide, or whatever we choose. That is the general outline on which the Committee is hoping to work. The intention is to use a heavily filled sole leather and a comparatively light unfilled; a belting butt, both curried and uncurried; some bag and strap leather, and so forth. In other words, the idea is to cover the ground as well as the number of collaborators makes possible.

I have outlined very roughly, what the Committee has in mind and have done it with the thought that possibly I might secure recruits for the Committee, because as stated a few minutes ago, the larger the number of men who collaborate in this work, the more exhaustively it can be done, and the less the need will be for repeating it in the comparatively near future.

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UNHAIRING OF HIDES AND SKINS BY ENZYME ACTION.*

By Chas. S. Hollander.

Probably the oldest method of unhairing was the process which is called sweating or staling of the fresh or soaked hides or skins. Originally it consisted of a rotting or fermenting process in piles of the hides, by which the epidermis and the hair follicles were attacked rendering the epidermis slippery and the hair in their sheaves loose, so that the hair will slip off; but when large quantities of hides had to be treated that way for manufacturing leather on the basis of production as it is now practiced, it was found that uniformly satisfactory results could only be obtained by closely controlling the temperature and humidity, as a fermentation process of this kind is a very ticklish one, since it requires constant watching and a very rigid adherence to conditions which after all were not too well defined. For instance, the temperature had to be kept very closely controlled because the bacteria which caused the right kind of sweating thrived best and most uniformly at their optimum temperatures, and under the most favorable moisture content of the air. It was found that they did not thrive so well in places which were subject to sudden changes in these conditions and for that reason, pits or chambers, so-called tunnels were constructed with insulated walls and they were kept warm by the admission of live steam and cool by water sprays as the requirements called for to insure uniform conditions of moisture and heat.

The hides were usually in these sweating tunnels for about four or five days until the hair began to slip. After unhairing, they were thrown into a weak lime liquor to plump or swell them which was deemed necessary for the subsequent steps. The sweating process alone did not plump the hides.

You will readily see that the man in charge of this step of manufacturing leather was at the mercy of good luck because if he happened to get hides badly infected with the wrong bacteria fermenting in them, trouble was sure to follow and the greatest difficulties were encountered with those strains of bacteria that do not only attack the epidermis and hair roots but also eat into

* Read at the Annual Meeting of the A. L. C. A. at Atlantic City, May 28, 1920.

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the grain and in that way cause irreparable damage. On the other hand, we are told that many an old tanner regrets the almost complete disappearance of this method of unhairing because certain great advantages were there to offset the difficulties. If the sweating process had been conducted correctly, then the result was a very good yield in weight and a superior toughness and strength of the leather. The explanation for this may be found in the fact that the bacterial action or more precisely, the enzymatic action on the hides opened up the pores and interstices and the result was that this opening allowed the scud to flow more freely from the skins. A hide properly opened up in this manner would take up the vegetable tannins better and more plentifully and result in high yields and great toughness.

The next oldest method of unhairing may have been the application of slacked lime. After the skins were brought back to their natural softness by soaking, milling and breaking, they were treated with milk of lime which caused the skins to swell and gradually dissolved the epidermis and the hair roots so that within one or two weeks, or for certain kinds of leather, a little longer, the hair could be readily scraped off. It has been stated that the action of sterile lime alone would effect unhairing, due to the dissolving action of the OH ions on the epidermis and follicles. This however, is hardly of practical interest since it would be manifestly impossible to run under sterile conditions. On the other hand, there is no doubt at all that the bacteria or rather, the enzymes generated by them in the lime liquors are indispensable for the right kind of unhairing action. One of the methods in use is to treat the skins first in an old used lime liquor. These old or mellow liquors contain a profusion of bacteria and all the products of their life process and among a great many of these is ammonia, which is due to the breaking down of the hide substance, and proteolytic enzymes. The action of these old or mellow lime liquors may be explained as follows: Into the original lime liquor a great many bacteria of such strains that will stand the alkalinity and can live upon the food offered them, *i. e.*, the digested keratin, gelatin and interfibrillary substance from previous batches, are continually introduced. They generate enzymes which soften and dissolve the substance of the epidermis and the hair follicles and also to a

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smaller extent the gelatinous and interfibrillary substance of the skin proper. We have been able to prove quantitatively in our laboratory, that a lime liquor about 2 weeks in use contains one-half as much proteolytic activity as the Oropon most commonly used for calf skins. The result is that the skin is opened up and made more accessible to the purely chemical action of the OH ions, which causes swelling and plumping. However, this swelling and plumping action is greatly restrained by the presence of colloidal matter. If the skins were left in this old and mellow lime too long the result would be an undue loss of hide substance, resulting in pipy leather, and a low, dull, indistinct grain with very little swelling and plumping of the hide; therefore, at the proper time, the process is interrupted by putting the skins into a fresh lime liquor in which the purely chemical action of the OH ions completes the swelling and plumping without any further attack of the hide substance. There is another process going on along with these which consists of the saponification of the natural grease of the skin by the caustic action of the lime causing the formation of insoluble calcium soaps which are however removed on unhairing and scudding. Here too, it is most advisable to have the skin properly opened up by the enzymatic action to assist the cleansing and scudding, which again is a most important factor in preventing spew later on.

Now let us consider what the result will be if we reverse the order of giving the old and new limes. The fresh lime which is practically free of bacterial enzymes and protective colloids exerts a strong and unrestricted plumping and swelling action. The result is that when these hides are treated afterwards in the mellow limes, the action of the enzymes cannot penetrate into the swollen skin and the result would not be so satisfactory because the natural grease would not be removed and the leather is not opened up to allow the free entrance of tannins. The surface or grain is therefore acted upon more strongly than the interior, which causes looseness or pipiness of the leather.

Sometimes and under certain conditions, the pure lime process is modified by sharpening with a little caustic soda which intensifies the plumping and the saponifying power of the lime. Caustic soda as in the Pullman process could be used for unhair-

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ing, but would not give any, or at least very little of the mellow lime action which consists of enzymatic activity and on the other hand, it would give too much gelatinous swelling, resulting in inferior strength of the leather. It would be effective in removing the natural grease very completely as the soaps thus formed are soluble in water.

Comparatively recently unhairing with sulphides such as arsenic, sodium and calcium sulphides, etc., have come into use, and for many purposes show good advantages. They are all strongly acting chemicals, whose chief characteristics are the tremendous dissolving action on keratinous compounds. They not only dissolve the epidermis, but under certain conditions the entire hair as well. Nevertheless, used with the proper precautions they give good results. Sodium sulphide is the chemical chiefly used, acting in water as a mixture of NaOH and NaSH. It is a very cheap article and cheapness and rapidity are the main advantages of this method. A solution of 2 per cent. or 3 per cent. strength is sufficient for dissolving the hair, which is a total loss. The grain is left rough and unsightly because the liquor can hardly be allowed to act long enough to dissolve out the hair roots. The most successful users of straight sulphide are the wool pullers who apply a strong solution of it either alone or in conjunction with some lime on the flesh side of the pelts but never allowing it to get in contact with the wool, which it would immediately destroy.

While sulphides are said not to change the actual hide substance in any way, there must be some action in rendering it more tender, for sulphided skins must be watched with a great deal more care during the subsequent bating than the limed skins. This according to my opinion, is the result of the strongly alkaline nature of the sulphide solution.

Calcium sulphides in one form or another are being used, but as far as I know, calcium sulphide alone is very little used in this country. Its action is similar to that of the sodium salt, in that it destroys the hair but it is milder on the corium and the process is slower. It is probably some calcium-sulphur combination when red arsenic is used in the lime liquor, and as only small amounts of red arsenic are introduced, it rather serves to quicken the action of the lime liquor without the characteristic dissolving

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action on the hair. It is claimed that by this admixture, a finer, cleaner grain and greater softness and stretch can be obtained in glove leather, as against straight lime. Correctly speaking, a straight lime is not used as often as one would suppose. Modifications can be easily introduced by the careful and discriminate use of small percentages of red arsenic, caustic soda and sodium sulphide in conjunction with the lime, the chief object always being to save time without sacrificing any desirable features of the finished goods.

To sum up, the hair is left in its natural condition of tensile strength of fibre and gloss, and the sweating or staling process if conducted properly, gives a strong leather and good yields. But the greatest disadvantage is that the process is extremely difficult to control. Besides, it does not give any swelling, plumping or degreasing action and for this reason, the process must be supplemented by the action of lime after unhairing.

The straight liming process has the advantage of comparative foolproofness in plumping, swelling, degreasing and cleansing. The disadvantages are slowness, difficult disposal of waste limes, high cost of labor due to handling and harshness and coarseness of the hair, which is often rendered brittle.

The advantages of the sodium sulphide process are cheapness and rapidity, since it can be used in paddles, while its disadvantages are that it is not foolproof in that the corium is more gelatinized and that the hair is a total loss. Besides, the disposal of the sulphide liquor presents great difficulties.

All the modifications of the liming processes in use, such as the addition of caustic soda, sodium sulphide and red arsenic to the limes do not materially shift the balance of advantages or disadvantages but I am informed that the use of these modified liming processes in paddles and drums is gaining ground with a great saving of labor cost.

I have outlined these processes of unhairing without making any claim to completeness in order to call your attention to a new process, which will solve a great many of the present difficulties.* The method depends entirely on enzyme action for unhairing. Of course, enzymes are really at work in all of the

* This process was invented and patented by Dr. Otto Röhm.

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sweating and liming processes heretofore used, because the bacterial action we have already considered really consists of the action of the enzymes secreted during their life process. But under practical conditions you cannot select the bacteria in such a way as to give you a certain required amount of enzymes. Therefore, it is indicated to use pure enzymes to start with, without relying on the rather elusive bacteria. Such enzymes are readily available in exactly determinable quantities and strength. The soaking, washing, milling and breaking is done as usual, and it is important that the skins be thoroughly soaked and soft. Then the skins are treated in a paddle with a weak caustic soda solution for one day, which causes the skins to plump and swell to the desired degree. This swelling in alkali like in the liming process serves to distend and separate the collagen fibres and helps the rapid penetration of the following liquors, after the skins are again brought down. Besides this action, the alkali disinfects the skins and reduces the danger of anthrax to a minimum. The second day the skins are brought down in the paddle by the use of bicarbonate of soda and treated with enzymes of exactly known strength which causes the solution of the epidermis and the hair follicles. On the third day, the skins are unhaired in the usual way and puered or bated.

This new process, seems to me, to avoid a good many of the disadvantages of the older methods; First, it is a rapid method taking only three days between soak and tan, while the sweating took 4-5 days, and the liming process from 5 up to 14 days according to the quality of leather, not to speak of the time consumed in bating and washing. Second, the waste liquors are clear and not putrid, and so easily disposed of, while the lime and sulphide liquors are a constant source of trouble. On the other hand, these great advantages are outstanding: First, once adapted to your particular needs, the process is as nearly foolproof as we could hope to make any, in that the amount of chemicals is small, the enzyme strength is exactly reproduceable, with sufficient latitude to allow for smaller variations. The work is done in paddles and therefore a great deal of labor in handling is saved. Second: By reason of the thorough opening up of the skins a much better penetration can be obtained resulting in a clear gain of strength, flexibility and toughness. Further-

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more, as another consequence of the better opening up, the natural greases and dirt are better removed, thus helping greatly in removing the chief causes of spew. Third: The hair is recovered with the beautiful natural gloss and absolutely clean and far superior in strength than by any other method except by sweating.

In concluding, I wish to thank Mr. Otto Haas for many valuable suggestions.

After completing his paper, Dr. Hollander made the following remarks:

I have had the privilege of seeing this process in actual operation, and I was struck at once by the great difference such a beam-house offers to the casual observer, as well as to the tanner, in comparison with the old liming method. In walking through the room where they conduct the liming process, you will find that lime is spilled over everything; there is quite a lot of smell and dirt and all kinds of inconveniences; besides, you see a great many workmen running around to plunge the hides and to move them and haul them, while in the beam-house that conducts unhairing and bating, by this new process, you will hardly find any laborers standing around; the work is practically done in the absence of anybody, and it is extremely clean and sanitary.

MR. VAN TASSEL: I would like to ask for some figures as to comparative cost.

DR. HOLLANDER: It costs about the same, everything considered. The great saving is in labor and time. The chemicals are so small in amount, that they hardly figure anyway. Now-a-days the chemicals are really a minor consideration, due to the fact that you can make your leather far faster and save labor. But, as I said, the cost is very small, and not greater than the lime treatment.

J. A. WILSON: Do you put the alkali, bicarbonate and the enzyme in the same water?

DR. HOLLANDER: No, first the skins are put into the swelling bath, and after the first day they are transferred to a liquor containing bicarbonate; that brings the skin down within a couple of

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minutes, say perhaps, ten or fifteen minutes, and then the enzyme is added.

We use an alkaline liquor of about 1½ per cent., and it is absolutely useless to recover that, because after a day or two you get strong fermentation, and the amount of alkali left in there would have to be titrated, so it doesn't pay to keep that little bit of alkali.

MR. WILSON: But you have the disadvantage of using a great quantity of water, and the disadvantage of two liquors instead of one.

DR. HOLLANDER: Well, you usually use more than one lime. I know some people keep the skins in the same pit and strengthen up their lime and plunge their lime, but a great many change their limes, and it causes so little trouble in changing the liquors there, that you can very well afford to run in more paddles, because at the same time you are running them through much faster. You see, this whole process of unhairing is done in two days.

C. R. OBERFELL: I would like to ask Dr. Hollander if this applies equally to light skins and to heavier hides ?

DR. HOLLANDER: Yes, it applies to both. Of course, you understand that in working with goat skins the application is a bit more severe than in working with calf skins and heavier hides. That is the only difference, however; otherwise it is exactly the same.

MR. OBERFELL: Have you seen sole leather made by this process ?

DR. HOLLANDER: I haven't seen sole leather, but I have seen the goat skins, and also the calf skins, and they compare in every way favorably.

MR. VAN TASSEL: I would like to ask Dr. Hollander regarding the flaccid condition of the hides; wouldn't that be deleterious to the operation of re-fleshing, or splitting ?

DR. HOLLANDER: I don't think you will find much difference there. I am not sure that that has been tried; I would not

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like to say anything definite on that, but if you split out of the first tan liquors, of course there is absolutely no difference.

MR. VAN TASSEL: I was speaking of a condition where it would be desirable to split in the green hide, ordinarily, in the lime condition, in which case the split would be tanned in bark.

DR. HOLLANDER: That I could not say; I am not familiar with it.

PRESIDENT GRIFFITH: Mr. Wilson, I think you have investigated the effect of ammonia in the beam-house.

MR. WILSON: I have done a considerable amount of work on unhairing by ammonia. If you take a perfectly fresh skin and put it in a dilute solution of ammonia, the hair will slip quite easily in the course of one or two hours.

Now, in practice you often run up against difficulties, and we made the discovery that, if you treat a skin with dilute acetic acid and then neutralize it, you get little or no unhairing with ammonia; but the great speed in unhairing with ammonia, with the fresh skins, would indicate that ammonia is a big factor in unhairing.

DR. HOLLANDER: Of course, Mr. Wilson, in your mellow liquors you have quite a lot of ammonia, and that no doubt helps. But why don't they use ammonia in a practical way? There must be some hitch.

MR. WILSON: I just mentioned this one: if the epidermis has had any acid on it previously, you don't get the unhairing action. There will always be some difficulty in getting certain skins that do not unhair readily.

DR. HOLLANDER: I would like to add further that the results are very uniform. Of course, it is preferable to conduct your unhairing operation so that the hair does not come off in the "Ara" bath, as we call it, because that would simply clog up your drains. They are left in such a condition that they come off in the unhairing machine. That is quite a little point.

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MR. WILSON: Have you done much work on varying the amount of enzyme ? Do you find that that makes any material difference ?

DR. HOLLANDER: We did that before we got onto a constant formula, but now we don't.

MR. WILSON: What effect did you find with increasing amounts of enzyme ?

DR. HOLLANDER: It makes it harder to control. You see, Mr. Wilson, there are several things that have to be considered in working out a formula for practical use. In the laboratory you can do all kinds of variations, and just as soon as your skin comes to the right condition, you simply grab it and take it out; but in the tannery you have to standardize your work, so that a certain operation will always have to occur at a certain time of the day, and this operation is so standardized now that it comes off every day at the same time, and the only factor that they have to vary in treating the different natures of skins is the temperature; the concentration of the bath and the time of action is absolutely constant, while the only variable is the temperature, and it is surprising to see how well you can control all your conditions just by varying that one variable.

MR. WILSON: Is there anything mixed with this enzyme, such as ammonium chloride ?

DR. HOLLANDER: Yes, sir, but not ammonium chloride.

F. S. HUNT: I would like to ask Dr. Hollander, if this process removes all of the fine hairs, so that it eliminates hand beam work ?

DR. HOLLANDER: Yes. Of course, in order to facilitate scudding, you are going to slate the skins just the same as before, but the fine hair comes off just the same as the other. However, just as in any other process, you will once in a while find a little spot untouched, and that comes off afterwards in the scudding, but the unhairing is just as satisfactory as by any other process.

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THE TIME FACTOR IN THE ADSORPTION OF CHROMIC SULFATE BY HIDE SUBSTANCE.*

By Arthur W. Thomas and Margaret W. Kelly.

A study of the time factor in the adsorption of the constituents of chrome liquor by hide substance has been reported.[1] The present investigation was undertaken to compare the action of pure chromic sulphate with that of chrome liquor and it is, therefore, suggested that the figures in the earlier paper be compared with the present one.

Materials Used.

A solution of chromic sulphate containing 2.185 grams Cr_2O_3 per 100 cc. was prepared by dissolving pure chromic sulphate in distilled water. The concentration of Cr_2O_3 in this solution after diluting 150 cc. of the solution with 50 cc. of water was approximately equal to that used in our earlier work.

Hide Powder.—A portion of the same batch of American Standard Hide Powder (1918) used in our earlier work was used in the experiments reported here. Upon analysis it showed:

	Per cent.
Moisture	13.32
Ash	0.28
Protein (N × 5.614)	86.85

Procedure.

In our previous experiments with chrome liquor, 200 cc. portions of the diluted chrome liquor were poured upon 5 gm. portions of hide powder in glass-stoppered bottles. These mixtures were kept at room temperature, agitated frequently, and filtered off at definite time intervals. They were filtered by suction on a dry paper in a Buchner funnel, and the chromed hide powder washed with 500 cc. of water which removed all the chrome liquor not chemically combined. The washed chromed hide powder was partially dried at 40° C. and completed at 100° C.

This method of pouring the solution onto dry hide powder failed to work in the case of pure chromic sulphate. The first set so run yielded figures which were very erratic; it was impos-

* Read at the Annual Meeting of the A. L. C. A. at Atlantic City, May 28, 1920.

[1] Thomas, Baldwin and Kelly. This Jour., 15, 147 (1920).

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sible to show any relationship between the amounts adsorbed at different time intervals. Not understanding the cause of the irregular results, the experiment was repeated resulting in discordant figures again, similar time intervals in the two sets being widely different. It was then decided to soak the hide powder in water before adding the chromic sulphate. This procedure gave concordant and regular results.

Five gm. portions of hide powder were placed in each of a series of glass-stoppered bottles, 50 cc. of distilled water added to each and allowed to stand over night. Then 150 cc. of the chromic sulphate solution were added, the resultant concentration of the solution on dilution with the water present with the hide powder being 1.639 grams Cr_2O_3 per 100 cc.

These mixtures were continually agitated and filtered off at the various intervals of time as noted below. They were filtered by suction on a Buchner funnel, the filtrate set aside for analysis and the chromed hide powder was washed with about 500 cc. of water to remove all the chromic sulphate not chemically combined with the hide substance. The washed chromed hide substance was then air dried.

The filtered liquor was analyzed for hydrogen ion concentration (immediately after filtration), Cr_2O_3 and total acidity. The chromed hide powder was analyzed for protein, ash, Cr_2O_3 and SO_3. The methods used are indicated in the paper lately published by Miss Baldwin.[2]

Measurements of the hydrogen ion concentrations of the filtered liquors were made immediately due to the slow hydrolytic change taking place in chrome liquors after dilution which results in appreciable changes in hydrogen ion concentration. To exclude the possibility of attributing changes of this kind to adsorption by the hide substance, a parallel set of measurements upon a separate portion of the chromic sulphate solution at the various time intervals was made. Any differences between the two curves are due to adsorption of acid by the hide substance.

Results.

The analyses of the dried chromed hide substance for each time interval are given in Table I. The analyses of the filtrates are to be found in Table II.

[2] This Jour., 14, 433 (1919).

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TABLE I.—THE COMPOSITION OF CHROMED HIDE SUBSTANCE AFTER VARIOUS LENGTHS OF TIME OF CONTACT WITH CHROMIC SULPHATE SOLUTION.

Time of contact	Protein per cent. (dry basis)	Cr_2O_3 per cent. (dry basis)	SO_3 per cent. (dry basis)
1 hour	97.80	1.51	3.15
2	95.83	2.17	3.69
4	93.42	3.75	4.65
6	92.41	4.50	4.90
8	90.61	5.33	5.49
12	87.97	6.26	6.38
24	84.32	7.70	7.40
48	83.76	8.46	7.91
72	81.52	8.87	8.56
96	80.84	9.19	8.89
8 days	79.10	9.91	9.51
16	78.15	10.13	9.98
32	76.69	10.74	9.96
64	77.75	10.71	10.16

TABLE II.—THE COMPOSITION OF LIQUORS[3] AFTER VARIOUS LENGTHS OF TIME OF CONTACT WITH HIDE SUBSTANCE.

Time of contact	Total acidity as gm. SO_3 per 200 cc.	Cr_2O_3 gm. per 200 cc.	Concentration of H^+ ion in moles per liter of filtrate	Concentration of H^+ ion in moles per liter in control liquor
0 hour	4.02	3.28	——	0.01413
1	3.89	3.22	0.00759	.01349
2	3.87	3.17	.00813	.01479
4	3.82	3.16	.00933	.01514
6	3.80	3.08	.01000	.01514
8	3.75	3.06	.01072	.01514
12	3.73	3.00	.01230	.01514
24	3.69	2.89	.01122	.01288
48	3.65	2.81	.00912	.01148
72	3.60	2.79	.00832	.00977
96	3.58	2.75	.00794	.00933
8 days	3.54	(2.80)	——	.00759
16	3.52	2.70	.00832	.00617
32	3.55	2.69	.00776	.00525
64	3.55	2.67	——	.00407

[3] An aliquot of the filtrate was taken for analysis in each case and calculated to 200 cc. of liquor, assuming (not correct, of course) that concentration was unaltered by contact with chromed hide substance.

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The changes in hydrogen ion concentration are shown graphically in Fig. 1. It is interesting to compare them with the curves obtained with stock chrome liquor, as reported in our previous paper. It will be seen that the trend of the figures is just the reverse in the two sets of experiments.

FIGURE 1

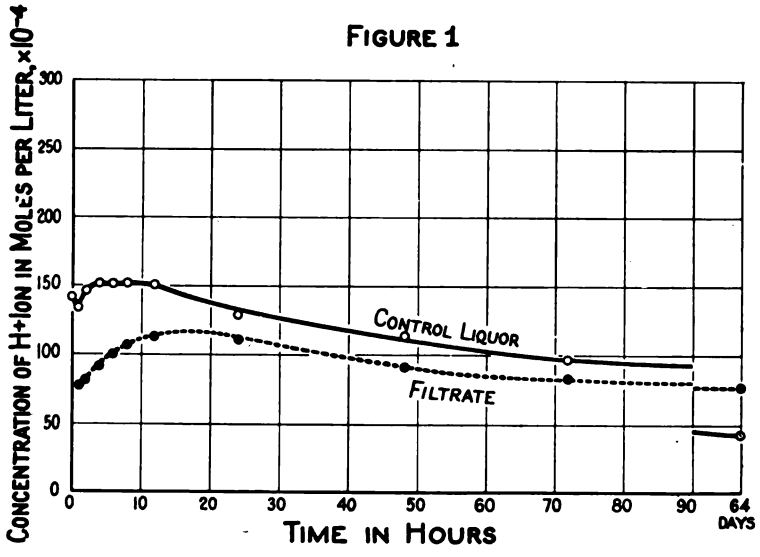

TABLE III.—AMOUNTS OF CHROMIC OXIDE ADSORBED BY UNIT WEIGHT OF HIDE SUBSTANCE.

Time	Milligrams adsorbed by 1 gram of hide substance: Calculated from analysis of powder	Calculated from analysis of filtrate
1 hour	15.5	12.3
2	(22.7)	21.3
4	40.1	(23.0)
6	48.7	38.6
8	58.9	43.0
12	71.3	55.5
24	91.5	77.8
48	101.2	93.4
72	109.0	98.1
96	113.9	105.5
8 days	125.5	(94.8)
16	129.8	114.1
32	(140.3)	117.5
64	137.9	121.0

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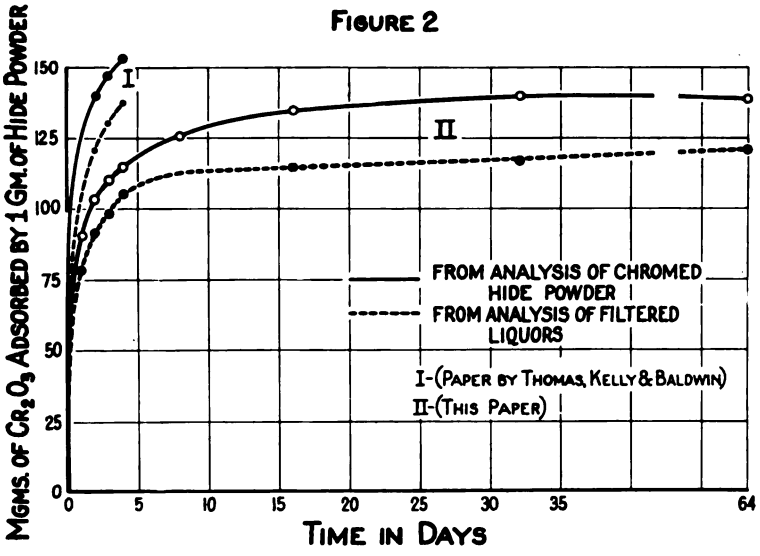
TABLE IV.—AMOUNTS OF SULPHURIC ACID ADSORBED BY UNIT WEIGHT OF HIDE SUBSTANCE.

Time	Milligrams adsorbed by 1 gram of hide substance: Calculated from analysis of powder	Calculated from analysis of filtrate
1 hour	32.3	25.8
2	38.6	30.6
4	49.9	39.6
6	53.1	45.2
8	60.7	(55.3)
12	72.6	58.2
24	87.9	67.3
48	94.6	75.0
72	105.1	85.9
96	110.1	88.3
8 days	120.4	95.5
16	127.9	(100.3)
32	130.1	94.2
64	130.9	93.4

FIGURE 2



Figures in parentheses are considered to be in error since they do not fit on the curves with the majority of the figures obtained.

The relations between the amounts adsorbed for different intervals of time as given in Tables III and IV are shown graphically below. For convenience of comparison the curves from our earlier paper are also plotted.

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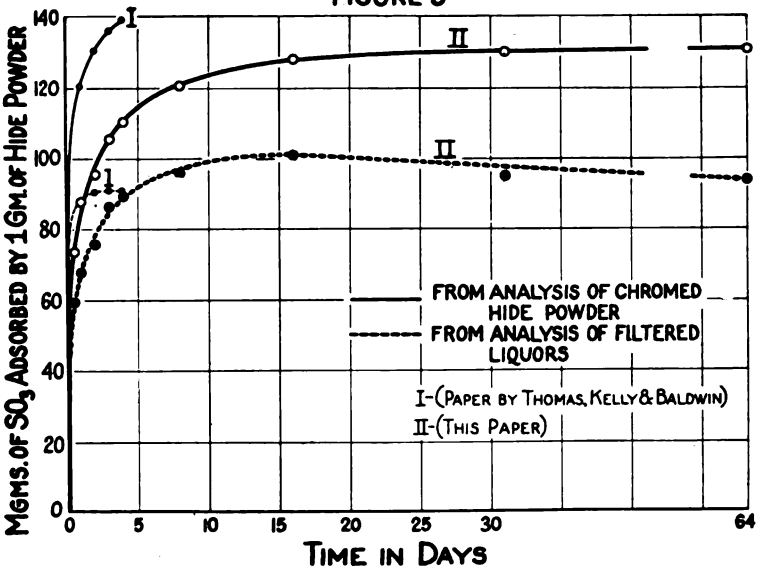
Between 32 and 64 days the chromic sulphate curves are flat, showing that the adsorptions are complete by that time. At completion 138 mg. Cr_2O_3 are combined with 1 gram of hide substance. Referring to the molecular weight of collagen as given by J. A. Wilson,[4] namely 750, this corresponds to a "tetrachrome" collagen. Miss M. E. Baldwin[5] in her study of the effect of the

FIGURE 3



concentration of chrome liquor upon adsorption by hide substance, setting the time of adsorption at 48 hours found 134 mg. of Cr_2O_3 to be the greatest amount that would combine with 1 gm. of hide substance, this corresponding to a "tetrachrome" collagen as well. This combination was obtained by shaking 5 gm. of hide powder with 200 cc. of chrome liquor containing 1.675 gm. Cr_2O_3 per 100 cc. Miss Baldwin found that less than 134 mg. of Cr_2O_3 was adsorbed when more concentrated chrome liquors were used.

Thomas, Kelly and Baldwin (*loc. cit.*), using this optimum concentration of chrome liquor, found however that for times exceeding 48 hours, more than 134 mg. Cr_2O_3 combined with 1 gm. of hide substance; at 96 hours it was 153 mg. Cr_2O_3 per

[4] This JOUR., 12, 108 (1917).

[5] This JOUR., 14, 433 (1919).

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1 gm. hide substance and the curve was still rising. These experiments have been extended to 64 days in order to reach the end of the reaction and to compare with the present paper. The results will be published shortly.

Inspection of the curves shows a marked difference between the speed of tanning with chrome liquor and pure chromic sulphate solution; the normal chromic sulphate tanning much more slowly and to a lesser degree than the basic sulphate, the reason for which may be found in the hydrogen ion concentrations which are about twenty times as great in the chromic sulphate solutions as in the chrome liquor.

Tables V and VI show the relative amounts of chromic oxide and sulphuric acid adsorbed at each interval of time. In Table V the relative amounts are calculated on the 96 hour basis, for purpose of comparison with the earlier paper, as well as on the 64 day basis.

TABLE V.—RELATIVE AMOUNTS OF Cr_2O_3 AND OF SO_3 ADSORBED AT EACH INTERVAL, IN TERMS OF—

Time (Hours)	Per cent. of total at end of 96 hours		Per cent of total at end of 1536 hours (64 days)	
	Per cent. Cr_2O_3	Per cent. SO_3	Per cent. Cr_2O_3	Per cent. SO_3
1	13.6	29.3	11.2	24.7
2	20.0	35.1	16.5	29.5
4	35.2	45.3	29.1	38.1
6	42.8	48.2	35.3	40.6
8	51.7	55.1	42.7	46.4
12	62.6	65.9	51.7	55.5
24	80.2	79.8	66.4	67.1
48	88.8	85.8	73.4	72.3
72	95.7	95.5	79.0	80.3
96	100.0	100.0	82.6	84.1
192	—	—	91.0	91.9
384	—	—	94.1	97.7
768	—	—	—	99.4
1,536	—	—	100.0	100.0

It will be noted that between 6 and 8 hours the ratio of equivalents of Cr_2O_3 and of SO_3 combined with hide substance is 1 : 2, or $1Cr_2O_3$, $2SO_3$ which corresponds with $Cr(OH)SO_4$. In our earlier research using a stock chrome liquor the composition of which was $CrOHSO_4$, this ratio of adsorption was obtained in 2 hours. In the chromic sulphate solution used in this investigation, the ratio of Cr_2O_3 to SO_3 was 1 : 3. Inspection of Table VI shows that this ratio in the adsorption was arrived at in just a

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little over *2 hours*. The coincidence is interesting although it is quite doubtful that any significance may be attached to it. As noted with stock chrome liquor, the acidity of the chromic sulphate solutions rapidly increases during the tannage.

TABLE VI.—Relative Amounts of Cr_2O_3 and of SO_3 Adsorbed as Per cent. of Total Amount of Both at End of Each Interval.

Time (Hours)	Cr_2O_3 Per cent.	SO_3 Per cent.	Ratio of equivalents Cr_2O_3 : SO_3
1	32.4	67.6	1 : 3.96
2	37.0	63.0	1 : 3.24
4	44.6	55.4	1 : 2.36
6	47.8	52.2	1 : 2.07
8	49.2	50.8	1 : 1.96
12	49.5	50.5	1 : 1.94
24	51.0	49.0	1 : 1.83
48	51.7	48.3	1 : 1.78
92	50.9	49.1	1 : 1.83
96	50.8	49.2	1 : 1.84
192	51.0	49.0	1 : 1.83
384	50.3	49.7	1 : 1.88
768	(51.9)	(48.1)	1 : (1.76)
1,536	51.3	48.7	1 : 1.80

The speed of adsorption has been tested by the mono-, bi- and trimolecular reaction formula, but it does not follow either of these simple reaction formulæ. The "constants" for the monomolecular formula are given in the tables which follow in order to compare Cr_2O_3 adsorption with that of SO_3.

TABLE VII.—Reaction of Hide Substance with Cr_2O_3 of Chromic Sulphate Solution.

$a = 655.5$ mg. Cr_2O_3.

Time (Hours)	x (Cr_2O_3 combined) mg.	$(a - x)$ mg.	$K = \frac{1}{t} \log \frac{a}{a - x}$
1	15.5	640.0	0.01039
2	22.7	632.8	0.00765
4	40.1	615.4	0.00685
6	48.7	606.8	0.00559
8	58.9	596.6	0.00511
12	71.3	584.2	0.00417
24	91.5	564.0	0.00272
48	101.2	554.3	0.00152
72	109.0	546.5	0.00109
96	113.9	541.6	0.00087
192	125.5	530.0	0.00048
384	129.8	525.7	0.00025
768	140.3	515.2	0.00014
1,536	137.9	517.6	0.00006

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TABLE VIII.—Reaction of Hide Substance with Sulphuric Acid of Chromic Sulphate Solution.

$a = 804.4$ mg. SO_3.

Time (Hours)	x(SO_3 combined) mg.	(a − x) mg.	$K = \frac{1}{t} \log \frac{a}{a-x}$
1	32.3	772.1	0.01780
2	38.6	765.8	0.01068
4	49.9	754.5	0.00695
6	53.1	751.3	0.00494
8	60.7	743.7	0.00426
12	72.6	731.8	0.00342
24	87.9	716.5	0.00209
48	94.6	709.8	0.00113
72	105.1	699.3	0.00084
96	110.1	694.3	0.00067
192	120.4	684.0	0.00036
384	127.9	676.5	0.00019
768	130.1	674.3	0.00010
1,536	130.9	673.5	0.00005

During the first and second hours, the speed of reaction with sulphuric acid is much greater than that of Cr_2O_3. This is similar to the results obtained by Thomas, Baldwin and Kelly with chrome liquor. There is an exception in that after the second hour the speed adsorption of SO_3 and Cr_2O_3 from chrome liquor are about equal, while with chromic sulphate solution it is observed that after the fourth hour, the speed of reaction of Cr_2O_3 exceeds that of SO_3.

We thank Mr. S. B. Foster for assistance in the analytical work, and express our great appreciation of the generous support of Messrs. A. F. Gallun & Sons Co., in this investigation.

Laboratory of Colloid Chemistry,
Columbia University,
New York City.

THE DETERMINATION OF TOTAL SAPONIFIABLE MATTER IN SULFATED OILS BY DIFFERENCE.

By Ralph Hart.

Rec'd. June 16, 1920.

In the Committee report for 1920[1] on the analysis of sulfonated oils, the total fatty matter varied from 1.17 per cent. to 1.97 per cent. from the actual values, and the Chairman concluded that only approximate results were possible by any of the present or proposed methods. He, therefore, recommended that total fatty matter "be taken as the difference between 100 and the sum of moisture, ash, unsaponifiable, ammonia and combined SO_3."

[1] This Jour., 15, 283 (1920).

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It would seem that the determination of fat by difference should yield good results, since the various items in the formula may be determined quite accurately. The above formula, however, as it stands, is applicable only to such oils which have been neutralized with ammonia alone, in which cases, none of the combined SO_3 would be found in the ash. Where a fixed alkali has been used for neutralizing, more or less of the combined SO_3 will be present in the ash, depending upon the amount of alkali. In such cases, the total fatty matter obtained by subtracting from 100, besides the other ingredients, both the ash and the combined SO_3 would be too low.

By using the methods for sulfated oils outlined by the writer,[2] and investigated by the above committee, it is possible to calculate, the exact amount of inorganic matter present in the oil, thereby remedying this defect in the above formula. The following inorganic matter is to be considered: (1) Na_2SO_4 and other foreign non volatile impurities, (2) neutralized combined SO_3 and (3) sodium and ammonium bound to soap.

The sodium sulfate and other foreign non volatile matter may be determined as described in a previous paper.[3]

The per cent. neutralized combined SO_3 is given by the formula:

$$\frac{NaSO_4}{SO_3} \times \%\ \text{combined}\ SO_3 = 1.49\ (\%\ \text{combined}\ SO_3)$$

For it must be remembered that the combined SO_3 exists as the neutralized salt, in the form R-O-SO_3Na—where R represents the fatty radicle. It is evident then, that in order to obtain the fatty radicle R, we must subtract $NaSO_4$, or one mole of $NaSO_4$ for every mole of combined SO_3.

Finally the per cent. alkali may be found according to these formulae:

$$\frac{NH_4}{KOH} \times \frac{A_1}{10} = 0.0322\ A_1\ \text{(for ammonia) and}$$

$$\frac{Na}{KOH} \times \frac{A_2}{10} = 0.041\ A_2\ \text{(for soda soap), where}$$

A_1 and A_2 represent the respective alkalies bound as soap, expressed in mmgs. KOH.

[2] This Jour., **12**, 189 (1917); **14**, 90 (1919).

[3] This Jour., **15**, 404 (1920).

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In the case where ammonia only has been used for neutralizing, the above formula for the neutralized SO_3 is not quite correct, as part of the sodium is replaced by ammonia. In the writer's experience, however, the sulphate group of every commercial sulfated oil, is practically all neutralized by the sodium from the salt used in washing the oil free of excess acid; a well washed oil requires very little alkali to bring it on the alkaline side. Furthermore, the error introduced by assuming all sodium even where ammonia might be present, is small as the difference in the molecular weights between them is not large and has only a small effect on the factor.

The presence or absence of foreign volatile matter such as alcohol, glycerine, etc., (which would seriously interfere with the result) could readily be detected as follows. Having found the weight of the fatty matter in the sample by difference, the saponification value of the sample is determined; the saponification value of the sample and the percentage of the fatty matter being known, the saponification value of the fat is readily calculated by division. As is well known, the saponification value offers the best criterion to distinguish saponifiable from non saponifiable matter. If the saponification value of the fat thus determined is too low, foreign volatile matter has been introduced; the sample is adulterated and special methods of analysis are required. The saponification value also serves as a guide as to the necessity to analyze an oil for unsaponifiable matter.

The corrected formula for total saponifiable by difference was applied to a few analyses on sulfated oils, reported by Dr. C. G. Bumcke,[4] with the following results:

	No. 3 Per cent.	No. 4 Per cent.	No. 7 Per cent.	No. 10 Per cent.	No. 13 Per cent.
Water	25.13	29.45	19.75	53.36	16.04
Neutralized combined SO_3	2.91	2.85	2.86	3.94	2.98
Ammonia	0.11	0.06	0.00	0.01	0.00
Sodium as soap	0.11	0.29	0.74	0.18	0.14
Foreign non-volatile[3]	0.86	1.57	0.67	3.25	0.17
Unsaponifiable	—	—	1.35	0.58	31.55
Total	29.12	39.22	25.37	61.32	50.88
Fat by difference, new method	70.88	65.74	74.63	38.68	49.12
Fat found (C. G. B.)	70.14	65.31	74.75	38.64	48.21
Difference	—0.74	—0.47	+0.12	—0.04	—0.91
Impurities and loss (C. G. B.)	0.97	0.49	0.72	1.18	1.01

[4] This Jour., 14, 515 (1919).

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The average variation between the fat by difference and that actually determined by Bumcke is in the neighborhood of one-half of one per cent. The new method in most cases gave the higher results, indicating that what is recorded by Bumcke as impurities and loss is probably fat lost by volatilization.

It is therefore evident that the total fatty matter may be taken as the difference between 100 and the sum of water, neutralized combined SO_3, ammonium, sodium equivalent to "alkali minus NH_3" and salts and impurities as suggested in a previous paper.

The writer would suggest that the following determinations be made in analyzing sulphated oils: (1) Combined SO_3, (2) soda bound as soap, (3) ammonia, (4) saponification value of sample, (5) non-saponifiable, (6) free fatty acids, (7) water and (8) ash. From this data, which for a pure sulphated oil would require, by the new method, about two hours to complete, the following could be calculated:

1. Total saponifiable matter.
2. Unsaponifiable.
3. Saponification value of fat.
4. Neutral fat.
5. Free fatty acids.
6. Fatty acids as soda soap.
7. Fatty acids as ammonia soap.
8. Combined SO_3.
9. SO_3 as salt and other non-volatile.
10. Water.

The formula for the determination of total saponifiable matter by difference as recommended by the 1920 Committee has been shown to be useful only in special cases, and an improved formula has been suggested which makes it applicable for all sulphated oils.

The writer is greatly indebted to Mr. G. W. Schultz, associate editor of this JOURNAL, for timely suggestions and helpful criticism.

New York, N. Y.

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ABSTRACTS.

Overheating Reduces Strength of Animal Glue. *Technical Notes No. 104,* Forest Products Laboratory, U. S. Forest Service. That long continued heating reduces the strength of animal glue solutions is demonstrated by the following test made at the Forest Products Laboratory.

Solutions of a high grade joint glue and a veneer grade glue were heated for 48 hours at 104°, 140° and 176° F., and tested every few hours during this period for strength and viscosity.

In the first 7 hours of heating at 176° the veneer glue lost approximately one-half its joint strength, and the high grade glue joints weakened almost as much. The greatest loss in the strength of the glue joints occurred at this temperature. In the solutions kept at 104° there was a sudden drop in the strength of the joints made with the high grade glue after 31 hours of heating, due possibly to a combination of bacterial and chemical action. The veneer glue joints showed a more gradual decrease at this temperature. The most favorable of the three temperatures tried was 140°, but even at this temperature an appreciable weakening in both glues was noted at the end of 7 hours, and longer heating caused greater loss.

The viscosity of the high grade glue declined more rapidly than that of the veneer glue, but at the end of the heating test the viscosity of the high grade glue still averaged higher than that of the veneer glue.

Covered glue pots were used in this experiment. When open glue pots are used the loss in strength caused by the heat is less apparent, since the loss is compensated to some extent by evaporation of the water. On the other hand, the concentration of the glue solution through evaporation is an expensive means of gaining strength.

Practical Method for the Extraction of Tanning Materials in the Tannery. By H. GIUSIANA, *Le Cuir,* 9, 189 (1920). The author recommends the use of a battery of vats containing about 150 gallons each, arranged with a wooden cover to keep in the heat. The vats are filled above a false bottom with tanning material. A wooden chute is arranged above the vats to distribute the liquors and another below by which they are run off into a tank where they can be heated and pumped again into the next vat. The first extraction is carried out cold and then the temperature is increased progressively for the succeeding vats. For pine bark and sumac the complete extraction should be carried out cold; pine bark liquors of 18° Bé. may be prepared in this way.

Recovering Chrome Salts from Old One-Bath Chrome Liquors. By H. GIUSIANA, *Le Cuir,* 9, 190 (1920). Considerable economy may be effected by precipitating used chrome liquors in a vat with milk of lime when insoluble chromium hydroxide is precipitated. The precipitate is washed by decantation several times, and then treated with 50° Bé. sulphuric acid to dissolve the chromium hydroxide. The solution should be heated by means of a steam jet and concentrated somewhat in order to obtain a

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solution of chromium sulphate free from calcium sulphate. This process offers the additional advantage that the sewage contains no chrome.

The New Nance Tanning Process—Vacuum Tanning by Pressure without Air. By W. J. THUAU, *Le Cuir*, 9, 282 (1920). The author describes a new improvement in the vacuum tanning process of C. W. Nance. It has been admitted that the vacuum tanning process tanned rapidly, but it did not give weight. This process takes ten days or longer to get the necessary weight. With the new airless process the same weight can be obtained in one hour provided the hide is tanned through, which ordinarily requires 4 days. As soon as a very high vacuum is obtained and all air is removed from the autoclave and hides, the pressure is applied with the result that the tannin is forced through more rapidly. All air is removed from the liquors and there is nothing in the hides to resist the penetration of the tannin. In tests carried out in England with autoclaves that could only stand 20 lbs. pressure, 60 lbs. green hides were tanned in three days, giving 70 lbs. finished leather. With an autoclave that will stand 60 lbs. it is hoped to be able to tan 80 lbs. green hides in two days.

By airless pressure as much weight can be obtained as by drum tannage, but without injury to the finished hides. Soaking of dry hides can be carried out in 24 hours without loss of hide substance, and hides, with the airless process can be limed in two days with comparatively no loss of hide substance.

The inventor claims that the process will soak, lime, tan, and dry hides in 14 days overall with a percentage of 60 from the green hides.

Drying Chestnut Extract by the Cardem Process. By H. M. CORMACK, *Trans. Am. Inst. Chem. Eng.*, 10, 411-38. In the Cardem process of drying, heated air, counter current to the combustion gases, is passed into a chamber with two floors, into which is atomized the liquor to be concentrated and dried. The fundamentals are in the proper circulation of the liquor into the chamber and the distribution of the heated air going into it. Efficiency tests were conducted and complete data including the quantity of coal burned, of air passing through the chamber, of the combustion gases discharged, temperature of heated air and combustion gases, analysis of coal and samples of extract, etc., for the calculations are given. From the results it is found that if combustion gases are used directly instead of heated air for the evaporation, higher thermal efficiency can be obtained without injurious results. Also it is found that the second floor is necessary in recovering lost material. The particular advantages of this process are: (*a*) Heated air and liquor are efficiently mixed; (*b*) as the liquor to be dried is atomized, the drying is greatly facilitated; (*c*) no fine powder is lost by being carried with the air currents, enough room being provided for the air to lose its velocity; (*d*) a special feature is that the dried chestnut extract does not become sticky on long exposure to air as it does by other drying processes, a result probably due to conditions of drying; (*e*) there is a high percentage of recovery of dry material;

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(*f*) the cost is low; (*g*) the atomizer can be arranged to be self-cleaning. In the Cardem process the liquor to be evaporated is atomized; so it is especially suited for those substances whose water inside the particles is to be evaporated. As in the case of chestnut extract, the water inside the particles is expelled, a fact revealed in the microscopical examination.

—*Chem. Ab.*

Manufacture of Chrome Suede Calf. By "NAPPA," *Lea. Tr. Rev.*, May 12, 1920. The very smallest class of market calf skins are recommended for this purpose, as a very fine texture and thin substance, combined with a moderate degree of tensile strength, are essential qualities. A larger skin would lose considerably by the splitting or excessive shaving that would be necessary. The skins required are such as are generally classified in most markets as "under 5 lbs.," these being the skins of very young or unborn calves, and possessing an exceedingly fine texture. On arrival at the tannery they may require a few hours' soaking in clean cold water to remove salt and any adhering dirt or blood. The removal of the hair will be generally accomplished by the use of common lime assisted by arsenic or sodium sulphide.

Deliming may be accomplished in several ways, but must in any case be carefully and thoroughly done, as the presence of lime would detract from the suppleness of the finished article. A bath of lactic acid will be found satisfactory, and will obviate the necessity for using the time-honored but very offensive bate of dog dung. It is also more subject to control, and therefore, is less likely to be a source of danger to the pelts. After fleshing the skins are run in a tumbler with clean water for 20 minutes or so, and then entered into the acid bath. The skins should be paddled continuously in this solution until delimed thoroughly. The point when this stage has been reached may be roughly gauged by an experienced workman by pressing the grain with the thumb, and if thoroughly done the impression of the thumb remains on the pelt. The skins have also become opaque in color, and "fallen," and flaccid in feel. When finished the skins should be given another drumming in clean water for a few minutes and horsed up to drain. In this drained condition they are generally weighed for the purpose of basing the calculations for the next operation, which is the chroming.

Preparatory to the actual chroming, the skins are paddled in a pickling solution composed of 5 per cent. of common salt and 2 per cent. of hydrochloric acid, based on the pelt weight, and sufficient water should be added to cover them. This assists a better assimilation of the chrome, and produces a soft leather. Having been paddled in the pickle for three or four hours, they are taken out and again drained. The chrome liquor may be prepared with 10 per cent. of chrome alum, estimated on the pelt weight, rendered basic by the addition of common soda crystals. When satisfactorily tanned the skins are well washed for a few minutes in a solution of water and borax, the latter being estimated at 2 per cent. on the original pelt weight.

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The next operation is shaving, and in order to get them into a suitable condition for this the skins are struck out on the machine and hung up for a few hours in a warm stove. They are required in a nice "sammed" condition—that is, not wet to the touch, but not baked up or too dry, as they would then be very difficult to wet back evenly again. In this semi-dry condition they are shaved on the machine, great care being taken to avoid marking them at all, as an absolutely clear, fine flesh is essential to produce a good-looking article. They will not, as a rule, need much taking off; the neck is the chief part where the substance needs reducing, but the skins must be a nice thin, even substance all over when they leave the shavers. They are next worked well over each skin on a carborundum wet-wheel, being pressed on to the revolving wheel by a pad held in the workman's hand. By this means the fine "nap" is secured, and this is very necessary, as, if it is not properly "fined" now, the subsequent operation of buffing, when dry, would only raise a coarse nap.

The operations of fat-liquoring and dyeing now follow, and the first stage, especially if the goods are being finished in a fancy shade of brown or grey, will be a mordanting bath. Cube gambier or fustic extract will be suitable for this purpose, and about 10 per cent. on the shaved weight of either (or a mixture of both) is dissolved in hot water (150° F.) and run into a drum through the axle. After running in this for about 20 minutes the skins are drained, swilled in clean water, or lightly struck out, and are then ready to receive the fat liquor. The skins are now ready for dyeing.

The composition of the dye bath may, of course, vary considerably, a number of shades being in good demand. Aniline dyes are now almost exclusively used for this purpose, and accurate instructions as to the use of these are sent out by the makers. On being taken out of the drum the skins are drawn through a tub of clean water, and struck out by machine. They may also be put through a samming machine at this stage if desired, and are then taken to the drying stoves. Here they are strained out by nailing on wooden frames, and dried in a fairly brisk heat.

The first of the actual finishing processes is softening by staking. On coming from the stove, the skins are laid in a bin and covered with damp sawdust, a layer being also spread between each skin. After three or four hours they will be in a sufficiently moist condition, and are then staked by machine. They are aired off in a slight heat, staked again, and then buffed on the flesh with a fine carborundum paper, either by hand or machine, thus raising the nap again. After this they are grained, by the board or by machine, in order to get a nice round grain on them. To give a final and complete softening, and to obtain a fine velvety feel, they are subjected to dry drumming. The goods are given twenty minutes or half an hour in this drum; a little French chalk may be thrown in if desired, and after removal from the drum they are given a good brushing by hand with a soft brush, and are then ready for sale. Measuring by machine should be done before the final brushing, so that the wheel marks may be brushed out.

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CONTENTS

Correction - - - - - - - - 503
Book Notice - - - - - - - - 503
The Determination of Sulfuric Acid in Leather. By Arthur W. Thomas 504
Titration of Chrome Liquors by the Conductance Method. By Arthur W. Thomas and S. B. Foster - - - - - - 510
Invention, Research, Engineering, Manufacture. By Buckner Speed - 516
The Determination of Moisture in Leather. 1920 Committee Report. By Robert Wright, Chairman - - - - - - 529
Abstracts - - - - - - - - - 534
Patents - - - - - - - - - 549

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G. W. SCHULTZ . . . . . Associate Editor

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CORRECTION.

In the committee report in the July issue on the Determination of Glucose, the paragraph before the last on page 422 should be omitted entirely. On page 425, the last point in the curve marked "(4) with NaOH" should be located at 8.14 per cent. instead of 7.68.

BOOK NOTICE.

The Editor has received A Guide to the Literature of Tanning and Leather Manufacture (Führer durch die Literatur der Ger-

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berei und Lederfabrikation) from Buchhandlung Schulze & Co., Leipzig, Nürnberger Str. 57, Germany. This is the most complete catalogue of books on the subject by German authors that has been brought to our attention. The literature is listed under the following general headings: Directories, Bookkeeping, Chemistry in the Tannery, Oak Plantations, Deliming, Factory Management, Dyeing, Fats, Oils, and Greases, Tannin and Tanning Materials; Historical and Political Economics, Fellmongering; Belting; Saddlery; Shoe Manufacture; Custom Duties; and Journals.

THE DETERMINATION OF SULFURIC ACID IN LEATHER.*

By Arthur W. Thomas.

A satisfactory method for determination of sulfuric acid in leather has been sought for years, but the aid of colloid chemistry has never been invoked. It seems to be fairly well established that ions are bound in so-called "adsorption-compounds" with jellies and gels in varying degrees of tenacity dependent to some extent upon the valence of the adsorbed ion. In general, the higher the valence of an ion, the greater is its precipitating power[1] toward a colloid of opposite charge and the precipitating power is a function of the degree of adsorption of an ion.[2]

Van Bemmelen[3] showed that a silicic acid hydrogel retained aluminum chloride so tenaciously that it could not be washed out with water, but, if the wash water contained some potassium chloride part of the aluminum chloride was removed and potassium chloride adsorbed in its place.

Whitney and Ober[4] found that, in the precipitation of arsenious sulfid hydrosol by salts of the alkaline earths, there always remained in the gel, depending upon the precipitating salt used, amounts of barium, or strontium, or calcium, which were chemically equivalent.

* Presented before the Section of Leather Chemistry at the 59th meeting of the A. C. S. at St. Louis, Mo., and before the 17th Annual Meeting of the A. L. C. A. at Atlantic City, N. J.

[1] Schulze, *J. prakt. Chem.*, **25**, 431 (1882); **27**, 320 (1883); **32**, 390 (1884).

[2] Bancroft, *J. Phys. Chem.*, **19**, 363 (1915).

[3] *J. prakt. Chem.*, **23**, 324; 379; 395 (1881).

[4] *Z. physik. Chem.*, **39**, 630 (1902).

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Frion[5] noted in the precipitation of barium sulfate in the presence of magnesium salts and of lanthanum salts, that lanthanum ions were ten times more strongly adsorbed than magnesium ions.

Paine[6] found that when hydrous cupric oxide sol was precipitated by sodium chloride the gel could be converted back to the sol by repeated washing with water which removed the adsorbed chloride. However, if the sol was coagulated by a sulfate, washing would not redisperse the gel until an excess of sodium chloride had been added to the gel, which replaced the sulfate and then repeated washing with water resulted in peptization.

Since there appears to be a relation between the valence of ions adsorbed and "adsorption affinity" it was thought that if a leather containing sulfate, were treated with a phosphate solution, the sulfate ion might be replaced by phosphate and so removed from the leather.

A few trials with acid sulfated hide powder and chromed hide powder digested at room temperature in primary potassium phosphate solutions demonstrated that the theory was correct. Since one might assume that an acid should be removed from leather by soaking in an alkaline solution, an experiment was tried where the acid sulfated hide powder was soaked in m/50 NaOH. This removed only a small portion of the sulfuric acid.

It was soon discovered that treatment with phosphate solution in the cold was not practicable, since in the case of some leathers it took as long as a week to remove all the sulfate as compared with seventeen to twenty-four hours for unfat-liquored sulfated hide powders and chromed hide.

Boiling the leather with the acid phosphate solution in a beaker was tried but proved unsatisfactory. From further experimentation the method described below was found to be the best.

Procedure.

One gram of leather is placed in a 250 cc. volumetric flask and covered with 200 cc. of a m/10 KH_2PO_4 (or NaH_2PO_4) solution.[7] The flask is immersed in a bath of boiling water for two

[5] *Jour. Chim. physique* **7**, 111 (1909).

[6] *Koll. chem. Beihefte*, **4**, 24 (1912).

[7] The amount of sulfate in the phosphate used should be determined. The KH_2PO_4 used in this work showed 1.0 mg. of SO_3 per 200 cc. of 0.1 molar KH_2PO_4 solution.

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hours. It is then cooled, made up to the mark with distilled water, shaken well and filtered through a folded paper. The first 20-25 cc. of filtrate are discarded and then 200 cc. of filtrate are collected in a 200 cc. volumetric flask. This solution is transferred to a 600 cc. beaker, 20 cc. of molar hydrochloric acid added, heated to boiling and the sulfate precipitated in the usual manner by barium chloride. A large beaker is used on account of the tendency to foam when the barium chloride is added to the hot solution.

This procedure gives total sulfates in the leather. From experiments with hide powders that have been treated with sodium sulfate and magnesium sulfate, it has been found that treatment as above described, using water in place of phosphate solution removes all neutral sulfate in forty-five minutes. The difference between the two digestions gives the acid SO_3.

If total sulfur be determined by the $NaOH$-Na_2O_2 fusion method, then the difference between the value for SO_3 so obtained, and that by the acid phosphate method yields the sulphid, "animal" sulfur and sulfonated oil sulfur in the leather. The conditions employed in this method do not hydrolyze sulfonated oils.

Total sulfates are accurately determined by this method but there is an unavoidable error in estimating the acid SO_3, because in the boiling procedure with pure water to remove neutral SO_3, a portion of the acid SO_3, about 7-10 per cent. of the total is extracted as well. Despite this error, this method is apparently much better than any proposed in the past.

For conservation of space, the many figures obtained in developing the method are omitted.

Leathers Used.

"B"—Chrome side leather, washed after tanning but not fat-liquored.

"C"—Sole leather.

"E"—Strap leather, vegetable tanned.

"F"—Chrome calf leather, fat-liquored with sulfonated neats-foot oil.

"G"—Chrome re-tan side. Chrome leather re-tanned with vegetable tanning materials.

"13"—Sole leather (shavings).

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"14"—Sole leather (powdered).

All samples except the latter two were cut up into small cubes.

Results.

For convenience in comparison the results are all calculated to SO_3.

	1 Total sulfates by peroxide fusion	2 Total sulfates by this method	3 Neutral sulfate by this method	4 Acid sulfate by difference between 2 and 3
	%	%	%	%
"B"	4.49	4.27	0.28	3.99
"C"	4.58	3.59	2.97	0.62
"E"	0.94	0.34	0.15	0.19
"F"	3.62	3.07	0.31	3.76
"G"	3.02	2.34	0.56	1.78
"13"	3.10	2.72	2.12	0.60
"14"	2.18	1.75	1.26	0.49

When the 200 cc. volume of digestion mixture is used, not more than one gram of leather containing over 5 per cent. SO_3 can be taken as shown by the following case which is typical of several others which have been observed.

A sample of chromed hide powder showed 6.86 per cent SO_3 by the peroxide fusion method. One gram digested with 200 cc. m/10 KH_2PO_4 yielded 6.40 per cent. SO_3 while 0.5 gram yielded 6.69 per cent. SO_3. Hence there is a definite equilibrium between the sulfate which goes into the solution phase and that which remains in the leather phase. Therefore, if it is desired to digest a sample greater than one gram, the volume of phosphate solution must be increased also.

It has been found unnecessary to extract the fatty matter from leather previous to digestion.

This method might also be used for the determination of hydrochloric acid and neutral chlorides in leather. Experiments are being conducted to test this assumption.

Book binders complain that modern leather is not so durable on books as older samples, possibly due to small amounts of sulfuric acid left in it. It is suggested that leather drummed in a phosphate solution before fat-liquoring would have all its free "mineral" acid extracted and replaced by phosphate. It would be interesting to see whether such leather would be more stable.

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The author wishes to acknowledge the generous support of Messrs. A. F. Gallun & Sons Co. and to thank Mr. John Arthur Wilson who kindly furnished the samples of leather.

(Contribution from the Chemical Laboratories of Columbia University, No. 339) New York City.

Discussion that followed the presentation at Atlantic City:—

MR. VEITCH: Mr. President, this line of work that Dr. Thomas has started, with regard to leather, is really an old line of work in connection with soils, and there we have found that it isn't only the valence that has to do with the matter—potassium salts will always replace more largely than will sodium salts, more largely than magnesium or calcium salts; and it occurs to me that perhaps you might get very satisfactory extraction by using potassium chloride, rather than the potassium phosphate—not that I see any objection to the phosphate.

DR. THOMAS: I tried sodium chloride, however, and I would imagine, from what I generally have in mind concerning the reaction of these salts with colloids, sodium chloride would probably give you the same effect in this case as potassium chloride.

I think I emphasized, in reading my paper, a number of dates around 1880, 1881 and 1882, showing that this material has been on hand now for about forty years, but has never been made use of.

MR. VEITCH: It has not been made use of for leather, necessarily, but it has been very extensively used in agricultural chemistry; and I still disagree with your statement that potassium chloride and sodium chloride will give results in the same magnitude. I am perfectly satisfied that potassium chloride will give higher results.

MR. SCHULTZ: Mr. President, I would like to ask Dr. Thomas about the titration of the aqueous extract to determine the amount of acid extracted; how will the titration be carried out? If it is made with an ordinary indicator, there will be considerable difficulty in titrating the aqueous extract of vegetable tanned sole leather, for instance, that contains about 20 per cent. of soluble matter. Otherwise I cannot see that the method is better than the modified Procter and Searle method.

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DR. THOMAS: Your criticism of titrating in the case of vegetable tan leathers is quite valid, because you have a dark solution there. There is no doubt but that it could be done with a hydrogen electrode, if that were necessary. But I have found in all cases, that the amount of acid sulphate that comes out with the neutral sulphate in the straight water extraction is from 7 to 10 per cent, (it has never gone below 7 or over 10) and while I don't suggest any rough approximations like that, I think it is better than the old ashing method, by assuming that 10 per cent. of the total acid sulphate is removed with the neutral sulphate in the aqueous extraction. I admit that the method is open to that difficulty in the case of vegetable tanned leather. With chrome tanned leather, it works beautifully.

MR. SCHULTZ: I would also like to know what effect the presence of magnesium sulphate would have on the extraction of acid by water ? Wouldn't sole leather with one per cent. acid, that contains no magnesium sulphate or no sulphates of inorganic salts yield different results from one with a relatively large amount of salts ? Could there be a constant factor under these conditions ?

MR. ROGERS: I would like to ask Dr. Thomas if he tried any experiments on a vegetable tanned sole leather by applying the method to the original sole leather and adding a definite amount of the acid ?

DR. THOMAS: No; my method of attack was always to take the American standard hide powder and dope it up. It would be rather difficult with sole leather; in passing through an acid solution, I would be at the same time washing out some other neutral salts, so I thought it was better to take the hide product.

MR. SMALL: Mr. President, has Dr. Thomas any opinion to give us as to how fine a state of division it is desirable for the leather to be in, to meet the conditions of the experiment ?

DR. THOMAS: I have tested that point and I found it didn't make much difference; cubes two millimeters in length would work; in fact, cubes four millimeters in length would work with

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this method. I had some leather shavings and some powdered leather. I have gotten satisfactory results with all of them.

MR. CREESE: I would like to ask if Dr. Thomas thinks a method could be worked out for hydrochloric acid ?

DR. THOMAS: I think it can be worked out on the same basis; in fact, I thought of taking that up.

MR. CREESE: You think the same principle would apply ?

DR. THOMAS: I do.

MR. FAUST: As I understand it, the bulk of your work has been done on chrome leather and hide powder. Do you think your method will be applicable to sole leather ?

DR. THOMAS: It would be applicable to this extent: that in getting your neutral sulphate out, the value that you get there will contain also about 7 to 10 per cent. of the total acid sulphate. Of course, when your sulphuric acid is one half of one per cent., ten per cent. of that is five hundredths of one per cent; so you would actually get by this method forty-five hundredths.

TITRATION OF CHROME LIQUORS BY THE CONDUCTANCE METHOD.*

By A. W. Thomas and S. B. Foster.

The determination of the "basicity" of chrome liquors is part of the routine control which is continually made in chrome tanning. According to the provisional method of the American Leather Chemists Association, the "basicity" is the ratio of basic radical to acid radical expressed as $\%Cr_2O_3/\%SO_3$ or sometimes $\%Cr_2O_3/\%Cl$. The acid determination is made by taking 50 cc. of a chrome liquor (of 0.15-0.25% Cr_2O_3 concentration), diluting with about 400 cc. water and titrating,, while boiling in a 7-inch porcelain dish, with 0.5 normal sodium hydroxide to the pink end point with phenolphthalein. The pink color must persist after one minute boiling. We have found this method to be tedious, of uncertain end point, and to give low results.

* Presented before the Section of Leather Chemistry at the 59th Meeting of the A. C. S. at St. Louis, Mo., and before the 17th Annual Meeting of the A. L. C. A. at Atlantic City, N. J.

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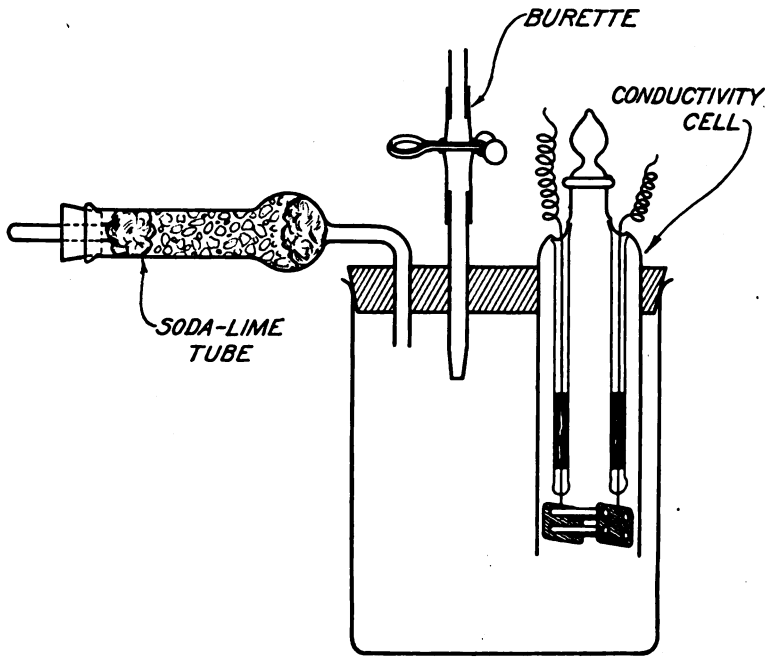
Attention was turned to a conductance method for this purpose and our early attempts were based upon the theory that the conductivity of a chromic sulfate solution should decrease upon addition of sodium hydroxide to a minimum at the neutral point, due to substitution of Na^+ for the highly mobile H^+ formed by hydrolysis of the chromic sulfate, and precipitation of

FIG. I



the Cr^{+++}. Then the conductivity should increase due to the OH^- and Na^+ added. These attempts proved discouraging because the turning point was not sharp. It was then found that Harned[1] had already successfully used such a method in the titration of the sulfates of magnesium, calcium, copper, nickel and cobalt, using barium hydroxide.

[1] *J. Am. Chem. Soc.*, 39, 252 (1917).

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Application of Harned's method to titration of chromic sulfate solutions has proven successful in our hands. As will be seen later, the turn in the curve is very sharp when barium hydroxide is used.

Apparatus.

Titrating Cell.—The bottom of a conductivity cell was cut out. This cell was then inserted in a large flat cork stopper which fitted on a 250 cc. lipless beaker. Two other small holes were cut in the cork. In one was inserted a soda-lime tube and the other served as inlet for the tip of the titrating burette. The whole set up may be more clearly understood from Figure I.

Other apparatus used were an ordinary Wheatstone bridge conductivity outfit and a temperature regulated water bath.

Reagents.

An approximately 0.1 normal barium hydroxide was made up according to Findlay[2], and standardized against benzoic acid obtained from the U. S. Bureau of Standards. 1 cc. of barium hydroxide was found to be equivalent to 0.0040 gram SO_3.

Procedure.

A chromic sulfate solution was prepared by dissolving 54.4 grams of crystallized chromic sulfate in a liter of distilled water. This solution was labelled "A". Solution "B" was prepared by diluting 50 cc. of "A" to 100 cc. with water and "C" was one quarter the strength of "A".

4 cc. of a chromic sulfate solution were pipetted into the titrating cell and diluted to 100 cc. with distilled water. The cell was then hung in the water bath (at 25°), the burette delivery tip inserted, and electrodes connected to the bridge. After five minutes, to allow the solution to arrive at 25° C., the null point on the bridge was found and the resistances manipulated so that the null point was located near the end of the bridge, in order that the readings during the titration could be made on the slide wire without changing the resistance box.

The barium hydroxide solution was added in 3 to 5 cc. portions, the solution in the cell shaken in order to ensure thorough mixing and the bridge reading for null point taken. When near the end point, the barium hydroxide solution was added in small

[2] *Practical Physical Chemistry*, 3d Edition, p. 162.

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amounts, 0.2-0.3 cc. at a time. Two or three readings beyond the end point were taken in order to determine the slope of the curve. Two titrations reproduced below show how the turning point is arrived at. The numbers of cubic centimeters of barium hydroxide are set opposite the bridge wire readings.

TABLE I.

Chromic sulfate solution "A" 4 cc. diluted to 100 cc.		Chromic sulfate solution "C" 4 cc. diluted to 100 cc.	
Cc. $Ba(OH)_2$ solution	Bridge wire reading	Cc. $Ba(OH)_2$ solution	Bridge wire reading
0	65	0	52.5
5	59.7	3	37.6
10	53.1	4	27.5
15	36.8	4.3	25.5
18	25.3	4.6	23.8
18.5	23.9	4.8*	23.0*
18.8	23.4	5.0	23.5
19.0*	23.2*	5.5	28.4
19.2	23.6	6	37.6
19.5	24.1		
20	25		

* End point.

These figures were set against each other on coördinate paper and the curves drawn as shown below. It can be seen that by this method one need not try to exactly reach the end point. Provided two or three further additions of barium hydroxide are made and the bridge readings noted, the end point is determined by the intersection of the two curves (actually nearly straight lines).

In regard to contamination by carbon dioxide, it was not found necessary to boil the solutions before titrating. It is merely required to exclude CO_2 during titration, which is accomplished by the cell described.

Since in the American Leather Chemists Association method for titration of chrome liquors with sodium hydroxide, it is necessary to boil during the titration to decompose the chromic oxide sulfate adsorption compound, it was decided to determine the significance of boiling, on the end point, in the barium hydroxide conductance titration. A solution was removed from the thermostat when the end point had been reached (but not passed), boiled, cooled to 25° C., and the titration resumed. The curve was altered a trifle in shape, but the end point was not changed.

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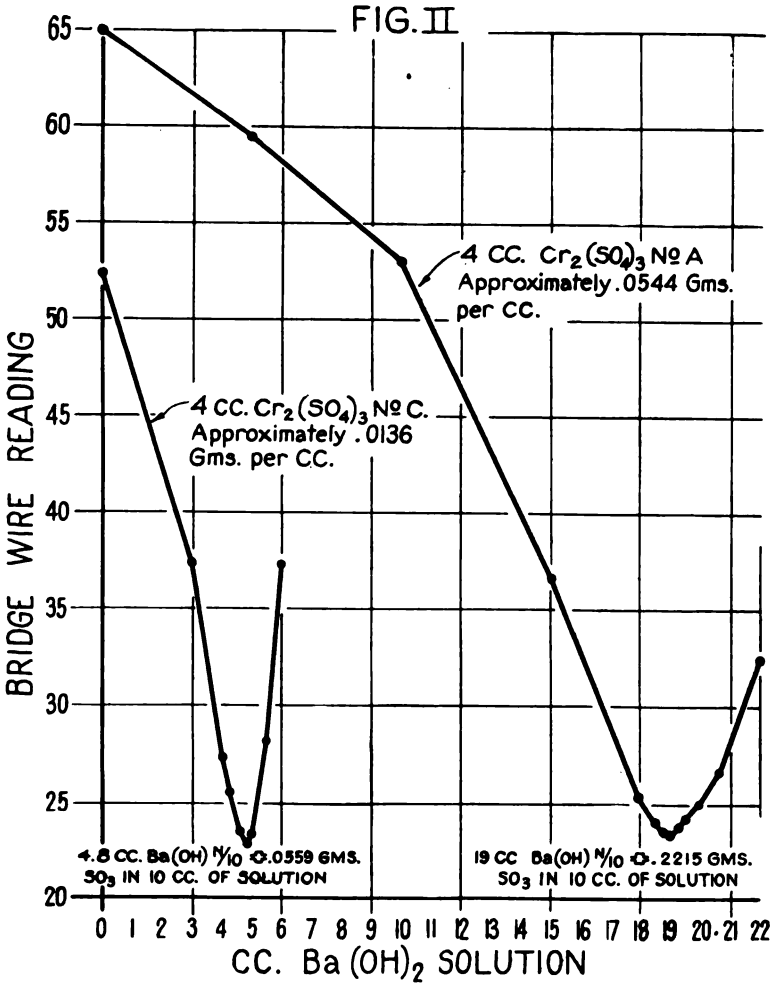
The figures submitted below show that there is no "adsorption" of sulfates in the hydrous chromic oxide precipitated by barium hydroxide. This is to be expected in consideration of the insolubility of barium sulfate.



Comparison of Methods.

For convenience in comparison with the A. L. C. A. method the total titrable acidity of the chromic sulfate solutions is expressed in terms of SO_3. For comparison, sulfate was also

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determined gravimetrically by the usual method of precipitation with barium chloride.

TABLE II.
Determination of Sulfate in Chromic Sulfate Solutions.
Results expressed in grams SO_3 per 100 cc.

	A	B	C
A. L. C. A. method.....	0.2121	0.1057	0.0540
Gravimetric "	0.2196	0.1108	0.0554
Conductance "	0.2215	0.1108	0.0559

The sodium hydroxide solution used in the A. L. C. A. titrations had been standardized against Bureau of Standards' benzoic acid.

It will be noted that the A. L. C. A. method gives *low* results compared with the other methods. We thought this might be due to chromic sulfate adsorbed in the hydrous chromic oxide precipitate which is present at the end point. To test this view, 15 cc. of solution "A" were titrated with NaOH by the A. L. C. A. method (boiling temperature) until the pink end point with phenolphthalein was obtained.

The hydrous chromic oxide was filtered off and washed on the filter with 700 cc. of hot water. At this point 100 cc. of the washings showed but a very faint cloudiness when tested with barium chloride, indicating that all the mechanically adhering sulfates had been washed away. One liter of cold water was then filtered through. We believed that the precipitate was free of any uncombined sulfate by that time and dissolved it in dilute hydrochloric acid. Barium chloride was added and a precipitate of barium sulfate equivalent to 4.8 mg. of SO_3 per 10 cc. solution "A" was obtained. This partly compensates for the low results with the A. L. C. A. titration method, and shows that boiling at the end point (as indicated by phenolphthalein) does not decompose the hydrous chromic oxide-sulfate "adsorption compound," *i. e.*, this adsorption compound containing about 3 per cent. of the total sulfate present is quite stable in solutions of $C_{H+} = 10^{-9}$ at boiling temperature.

In comparing the conductance method with the gravimetric, it will be noted that they checked each other in the cases of solutions "B" and "C". A high result is noted for the conductance titration of solution "A", and this is illustrative of our experience with solutions more concentrated than "B"; the sharpness of the end

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point decreases with increase in concentration of the solutions titrated. The maximum concentration consistent with accurate results should not be greater than 1 gm. $Cr_2(SO_4)_3$ per liter.

This method, like any other, gives good results only after the operator has had some experience with it. With practice the change in conductance due to addition of 0.1 cc. n/10 barium hydroxide can be detected. A few trial titrations must be run, after which the titrations can be carried out with great facility. When the approximate acidity of a given chrome liquor is unknown, it will be necessary to run a rough preliminary titration. If the titrations are run at room temperature (without temperature control) the curves are irregular and the end point cannot be accurately determined.

Conclusions.

The conductance-barium hydroxide titration of chrome liquors and chromic sulphate solutions gives results which in general agree with the gravimetric method.

This method is to be preferred to the A. L. C. A. titration method, not only on account of theoretically truer results, but due to its convenience. It takes 20 minutes for a titration and boiling is not required. With improved apparatus, several samples can be titrated simultaneously.

We take pleasure in acknowledging Messrs. A. F. Gallun and Sons Company's support in this work.

(Contribution from the Chemical Laboratories of Columbia University, No. 340) New York City.

INVENTION, RESEARCH, ENGINEERING, MANUFACTURE.*

By Buckner Speed.

The steps by which a new thing makes its way from its conception to its quantity production are invention, research, engineering, and manufacture.

With the coming of the larger enterprises these steps instead of being carried out by one person are now usually separated and in the hands of quite different people. Each step has gone through much specialization, increased certainty of result has been obtained, and much of the gamble has gone out of invention.

* Read at the annual meeting at Atlantic City, May 28, 1920.

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Definition of these words is not very profitable—invention, research, engineering, manufacture. The Supreme Court has not been able to give a definition of invention; but usually the first beginning from which a new thing comes into being is the question "What will happen if such and such a thing is done ?" The state of mind causing this valuable query may slowly result from an intimate knowledge and close acquaintance with the general requirements of the case, or in some instances the question "What will happen if we do so and so" is the result of the first impression produced upon one who for the first time becomes acquainted with the inner detail working of a factory and therefore sees it in a somewhat unusual way. This is one of the advantages of calling in a consulting engineer.

The United States Patent Office holds that an invention has been "reduced to practice" in the meaning of the law when a description of the invention, sufficiently complete to enable one skilled in the art to practice the invention as instructed by the inventor's description, has been filed, even though the inventor has never practiced it himself.

Following the inventive act comes research, by which, first of all, the state of the art, as it is called, is sought. In chemistry much can be obtained from the vast abundance of well indexed literature available in all the large universities and in some public libraries. To get the information, however, one must be able to read more than one language, as these original sources of information are usually in the native tongue of the worker, and a great deal is lost in translation.

In some lines, for example machine design, most of the recorded sources of information are unfortunately in the crabbed language of the patent specification, and that literature is, unhappily, although probably unavoidably, in such a condition, that it takes an expert searcher in Washington who has access to the Patent Office indexes to run down the "State of the Art" as recorded in the United States, and foreign patent specifications.

The New York Public Library at Fifth Avenue and Forty-second Street has the complete American and British patent specifications and drawings,—several thousand large volumes in a good state of preservation and availability, but there is no subject index as at Washington and consequently unless one has the refer-

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ences from some other source, there is no way of making a first hand search there.

The purpose of research is to endeavor to find out, either from some printed record the experiences that others have had who have worked in the same field or to obtain the information through direct experiment in the laboratory often guided by mathematical analysis and extending it may be over months, or even years, keeping in touch the while with all the current scientific publications bearing on the research in hand.

The object of all these endeavors whether in libraries or laboratories is to get the answer to the original, germ question "What will happen if, etc.?"

After the original question "What will happen" has been answered hopefully through the agency of research, and quantitative relationships have been discovered or established through laboratory and mathematical research, showing under what conditions and in what measured ways or at what costs and economics the proposed new thing or method may be made to operate, there is next brought into play what is called engineering, which may be thought of as the quantitative application of experience in other parallel lines to getting the new scheme into practical working shape, the scheme whose suggestion, workability, and general rules have been obtained through invention and research.

Engineering, strictly considered, is probably a less exciting game than either invention or research, though more so than the next step, manufacture. Of course, if we all had to stay within our labeled professions like labor unionists, and if the engineer were forbidden to practice any of the other coordinated branches of development work, even as the plumber is forbidden by his brotherhood to bore a hole through a wooden floor; we should be unhappy indeed; but as we all know, all four of these overlapping fields of effort, invention, research, engineering and manufacture are constantly practiced simultaneously by the same individual.

I hope no one will take me to task on the division of the general field of development as I have laid it out. There are no more sharp lines of demarcation between invention, research, engineering and manufacture than between babyhood, childhood, youth and maturity, although each is sufficiently definite in our minds. There would be no particular advantage in wasting words over

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definitions were it not that in the development of large enterprises it has become the custom to parcel out large spaces for these different endeavors and to specialize them to the extent of employing groups of men to devote themselves almost exclusively to these separate subdivisions.

In most of the small companies invention is frequently either the incidental, or the leisure amusement of the active officers or superintendants who are closely in touch with the details of the manufacture, but also the requirements of the mercantile and financial side of the business. In many companies the business itself is the elaborate development of some single pioneer invention into a highly perfected manufacturing organization with no thought or particular care for anything else, other than through research and engineering (and minor invention that closely blends in) to perfect and cheapen the processes of manufacture of the original invention, or to so control the raw materials and inspection during manufacture that reliable excellence and uniformity of product is attained.

It was only a few years ago that most businesses scoffed at anything other than manufacture, and were rather given to resisting improvement that necessitated change of method or machinery; believing that it was better to continue manufacturing along the line that had paid so well in the past.

The tendency of the last four years is toward the establishment of research organizations in almost every company, so that every little factory has somewhere, chucked away in a corner, a place bearing the name of "the laboratory" and in it a college graduate who does some chemical control, or research, some inspection, some drafting, and often from his all around understanding of the business he accomplishes a surprising amount to the benefit of the company.

Besides this there are springing up all over the country semi-public testing laboratories, and research and development engineering laboratories, reaching a high point of organization in the great Mellon Institute at Pittsburgh. Without too much stretch of the definition we may even include the famous Rockefeller Institute for Medical Research in New York City under this head as its highest and most refined example.

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The function of some of their laboratories is to take the inventional idea of the factory man or some novel idea that he wishes to have investigated and under a stipulated arrangement perform the acts of research and engineering and turn them over for adaptation into the existing factory.

In all of these developments of the last dozen years, it will be seen that the stress has been on research and engineering (in main at least) rather than upon invention. In some quarters invention is actually frowned upon, it being thought the safer course of development lies in starting a well equipped body of investigators to run to earth all the possibilities of development through a study of what others have done elsewhere, and in the painstaking, inch by inch improvement of processes already shown to be fundamentally good. This research method, which was formerly called the painstaking German method, has proven of inestimable value, and does continue to yield almost invariably profitable results whenever it is faithfully followed.

It is, however, not often through such methods that the greatest improvements are obtained. The starting point for a new departure which leads into something genuinely novel the pregnant "What will happen if we do so and so" does not as a matter of fact and experience seem to occur naturally to the mind of a man whose pleasure lies in strictly research work, and who has specialized on a single narrow line. It has become a truism that pure mathematicians rarely make great discoveries in physics, there being of course notable exceptions.

The type of development and improvement that occurs directly in the factory, and which is suggested by the workmen, usually confines itself to improvements of the detail steps of the manufacture and it cannot be denied that often these improvements are valuable. Such improvements will enable a business to continue in competition where without them it would fall behind its rivals; but sooner or later mere improvements in details of manufacture will not save any business from some fundamental new invention undermining it. The dreaded invention may go so far as to be a total substitute for the thing manufactured, better either in point of cheapness or serviceability. No amount of improvements on carbon filament incandescent bulbs was able to save the great carbon-filament-lamp industry from extinction when the tungsten

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(or "Mazda") lamp had been brought into being; and the story of the development of metallic tungsten capable of being drawn into a wire suitable for lamps is one of the most brilliant tales of invention, research, engineering and manufacture.

There is actually some advantage in having the laboratory devoted to fundamental development work located quite out of the atmosphere of the production factory, in spirit at least if not geographically, because it is always possible to abandon the old and build a new factory, if need be, while if development is constantly being hedged in by the possibility of this or that machine or process, it is likely to be retarded.

I have heard that one of the great rubber tire companies proposes building a factory near New York which in a sense is not a factory at all, but merely a laboratory large enough to enable any inventional idea to be rapidly turned into actual full-sized tires which may be put to service test under close observation, the ruling idea in this enterprise being that nothing in any of their great manufacturing plants shall be regarded as restrictive to new departures, and that whatever machinery is required to put the novel idea to test will be built rather than modify the idea to fit their half dozen great production plants.

For many years one of the large electric companies has obtained most excellent results through the following sequence of operations. First the inventor conceives, either at his own initiative or as the result of a problem being set for him, what seems to him and to his co-workers a valuable idea. He submits a written statement of it to the company's patent department; this very quickly gives him the state of the art so far as recorded in the patent literature. The Company's Library Department, through the use of its own extensive library and through familiarity and utilization of the New York Public Library and the libraries in the Engineering Societies Building and the Chemists Club of New York, enable him or his assistant to run down the literature there available. Concurrently with this, actual experimental research is begun. I am inclined to doubt the wisdom of the inventor himself cooling the eagerness which comes with the first conception of an idea, by prolonged library work, and believe better results are obtained by his delegating the library work to others and letting them tell him day by day what they have found in the literature.

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Presently from preliminary experiments, enough proof of the workability of the original concept is obtained to warrant a small appropriation to cover the realization of the invention as developed by the original research, and for the quick realization of this a very thoroughly equipped shop employing several hundred men has been made a part of the laboratory building. The engineering planning and drafting and execution of the formal experiment is performed by still other experts in those lines, always under the direction and interest of the original inventor. Upon the completion of the model plant or apparatus its workability and characteristics are determined, in most cases not by the inventor himself, although he follows the work with great interest, but by a squad of men who have sometimes been called Doubting Thomases, and who most valuably serve the purpose,, through prolonged experience in the specialty of finding both the good points and the faults, and, not being biased in favor of the newborn thing as is the inventor, thus affording an incentive to the inventor without allowing him either to rest satisfied with what he has already achieved or to unduly discourage him on account of difficulties. Very frequently the modification which turn failure into success is made by these very Doubting Thomases themselves.

The laboratory shop model having passed through a long course of examination and attention from the inventor and the research men who have studied its theory and quantitative characteristics and the engineers who brought it into being, and the doubting Thomases, is then sent as a finished model to the factory, there to be studied by the proper officials in order that they may construct the necessary machines and tools for the manufacture of the new article in vast quantities. Here appears the great value of the separation of the development laboratory from the manufactory. I have been present at some of the inquests held over the laboratory shop models. Bright-eyed, kindly faced gentlemen hold the toy in their hands, with a more or less amused smile and occasional perceptible shakes of the head, and then with flash after flash and a twinkling eye, come dawning ideas, come the germs of the modifications necessary and the machinery needed to build the proposed article. Of course the manufactured article never looks like the thing the inventor imagined; but it functions in the same way and is in the end essentially the same.

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I believe in the high desirability of having the three original steps of invention, research and engineering unhampered as far as possible by the manufacturing exigencies so that the utmost freedom of imagination and ingenuity may be utilized, resting in the certainty that when the manufacturing experts finally get their hands on the laboratory shop model, they will be thoroughly competent to take all of the unpracticalities out of it and be able to either adapt it to existing machines or build new machines which will do something quite equivalent and usually better than the laboratory shop product with all its painstaking hand work.

Now the development of any inventional idea from its very inception has a number of alternatives open to the inventor. His point of view as to the means of realizing his desires are probably broader in the first days of his conception than later. He turns over in his mind the various ways of attack and finally settles upon certain of them, and, it may be, quite forgets the alternatives he might have followed up and as months pass and he or others are in the thick of research work, the other ways that might have been followed up are lost. It is therefore of the greatest importance that upon the conception of any new idea the inventor should, in the broadest way possible, in a thoroughly informal, gossipy, "letter to his brother" style of statement, put down his thoughts, putting them down, not so that he himself or someone else skilled in the game can understand them, but to the best of his endeavor try to tell his hypothetical brother who might be engaged in some unrelated business in the next town, what he has thought, and try his level best to make that not very bright brother understand. He will then do two most valuable things to the embryonic invention. He will not only get on paper a real description of what is in his mind, but he will amplify and broaden his own ideas to an extent scarely believed until one has tried it. He should sign, date and have witnessed every page of this statement. In addition to this somewhat diffuse letter, the inventor should early practice the compression of his inventional idea into the language of the patent claim. This is extremely important, as it forces him to think clearly and analytically upon what is the essence of his invention, and this again reacts on the broadening of the idea.

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The following is a form I have found works well as a guide to carry out the foregoing ideas:

Inventions are generally complete, so far as the patentable novelty is concerned, in a very few moments after the beginning of their conception. An invention is not a finished machine. Invention is not related to reduction to practice. The invention of an improvement in any machine, or device, or method, may not be operative, or it may not be valuable, but its invention is complete within the few moments that it occurs in the mind of the inventor. Consequently it is rare that joint invention occurs. When it does occur it is commonly brought about during a discussion which is directed toward a desired improvement.

As soon as an inventor has conceived an inventional idea it is his duty to prepare a letter to me, couched in about the following terms:

"My invention is an improvement in bookcases. It relates to the adjustability of the shelves of bookcases, and I conceive the essence of my invention to be a use of shelves which rest on wooden pegs which are stuck in suitable holes along the inside walls of the bookcase. The accompanying sketch, with complete descriptive notes thereon, is in itself, apart from this letter, sufficient to entirely disclose my invention in one of its workable forms."

"I suggest a claim reading somewhat as follows: A bookcase having movable shelves, the shelves supported upon pegs which are capable of being put in holes at various heights along the inside of the bookcase.

Signed: John Smith Dated:.....
Witnessed William Smith Dated:.....

The drawings should also be signed in ink with the full name of the inventor and dated, and witnessed with the full name of the witness and dated.

Upon receipt of the inventor's letter, which must be initialed by his supervisor and sub-division head, I will, as soon as possible, study the letter and if desirable confer with the inventor and, at as early a date as is convenient, put the matter up to the Patent Department in the usual form. This statement of invention must be drawn as promptly after the conception of the invention as possible and consultation with the patent attorneys, in most

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cases, can be well deferred until after this statement has been reduced to writing by the inventor. The purpose of this last remark is to save delay in reducing the patent conception to a written form, and for no other purpose. The patent attorney should be seen by the inventor within twenty-four hours after the moment of his inventive act if possible. At this point of the development it is well that the inventor should take his statements, with whatever sketches or other plans he has in mind, to the best and most experienced general patent attorney that he can find.

On presentation of the idea to him, he has recalled to his mind a great number of similar ideas—not that would seem similar to the inventor, but that classify themselves in the attorney's widely experienced mind as similar. I have been greatly interested, and immensely helped, by some of the older general patent attorneys in this way and have some doubt as to the advisability of the patent organizations which are built up by the in-breeding process of taking young men and training them to that special branch of the patent lore, which interests only one particular company.

A considerable proportion of inventional ideas are qualitatively sound, whether novel or not, but they may not be quantitatively valuable. Not only through research do we determine the novelty of the idea and obtain assistance from the work of others, but through research experiments, and analysis we are enabled to determine whether the inventional idea is quantitatively valuable. Mathematics is after all only quantitative logic. Through practice in the application of the mathematics to research problems, one acquires the ability to forecast whether or not a result depending upon a cause will be related to that cause in a simply proportionate way, or whether the result will be one of diminishing returns in proportion to the increase of cause; or of rapidly augmented result with increase of cause, or whether there will be maximum and minimum points in the results produced, as the amount of the cause is increased. God grant that some day public men and politicians may come to see this. Of course with scientific men this is so self-evident that it seems a waste of time to mention it, but to many a man it is not clear that in the affairs of life the result is not in direct proportion to the effort, no, not by any simply relationship.

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I believe that one of the pitfalls to be avoided in research work is the too early attempt to reduce the consideration of a question to the formal symbolic expression, because in so doing we perforce suppress many of the elements of the problem and these, while properly suppressed for the expression of the idea as conceived at that moment, may give a wrong decision with the apparent validity of mathematical certainty, because some of the elements will be forgotten through their suppression, instead of being augmented to a point when they become the controlling factors, and quite tip the beam from failure to success.

A number of illustrations of this might be called to mind. The discussion of forty years ago over epicycloidal or involute gear teeth, and the adoption of involute teeth because of the difficulty then existent of not being able to get the shafts at any exact distance apart and the consequent adoption of the more easily assembled involute gears over the actually better working epicycloid gears was followed later by the mathematical decision as to the best generating angle of the involute teeth, and this was again decided upon a basis which seemed valid then and which stood for many years until the pressure of the automobile industry produced a complete revision of gear tooth design.

The automobile industry in the same manner brought in a revision of the mathematically determined best shapes of screw threads, until now the Whitworth standard and the Sellers standard are only names of certain sorts of screw threads, and not final standards.

There is of course in manufacture an enormous temporary increase of profits through standardization, particularly where, by reason of patent protection a temporary prevention of competition can be obtained long enough to enable a stable business to be built up. But I have no undue admiration for the present day rage for standardization and would note that while through the standardization of the kodak and its films it was possible for me to buy films for my kodak all through Central America, Japan and China. Nevertheless the greatest development in hand cameras until recently was made outside the United States, as was also color photography.

The word standardization suggests the never ending controversy over the metric system. I shall not drag this in by the ears

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further than to register my own dislike of it, and hope that it will not be forced upon us through legal means. I merely mean that I do not care by law to have somebody else's preference forced upon me, whether the measurements amount to centimeters or three fingers.

At Miyiajama in Japan there is a beautiful old stone gate or tori which stands near the center of a very quiet lake, in whose surface the surrounding mountains are mirrored. The Japanese pilgrim is told to stand with his back to the view, bend over until his head is between his knees and then look at the view thus seen upside down. It is actually different when so looked at upside down, although to me it was not more beautiful. Now it is this ability to turn things upside down or stand them on their heads to get an unconventional point of view of a question which is of enormous inventional value. To illustrate, suppose I wish to invent or design a needle-threader. The obvious method is to hold the needle still and poke the thread through the eye. The stood-on-its head method is to hold the thread still and to poke the eye on to it.

In the matter of actual laboratory work, I am afraid it is historically true that the best work has been done in buildings that were none too fine. The huge cold vaulted ceilings and white enamel bricks of many a fine new University, have a chilling effect upon me. I somehow felt that in such a laboratory the sweeping and garnishing which has to be done, to be in keeping with the perfection of the place, would be harmful to actual warmth of work. In the matter of observing an experiment, long experience has taught me, both for myself and for those whom I have directed, that the actual work of observation should take place under conditions of the greatest possible bodily comfort, both as to position of body, quiet and light. All the pencil records taken during experiments should be of the simplest possible form, even though they are being computed as fast as the experiment proceeds, in order that the final answer may be obtained for modifying the experiment during its progress. I mean that the observer should either put down or call to someone else to put down exactly the thing that he sees, without any inferences such as subtractions, multiplications or estimates. The reason for this is that in this way there is the least chance for error and the observer is left

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free to do the very important thing of observing any chance occurrence during the experiment. It is easy to get, at a very low cost, plenty of laboratory workers to do exactly as they are told. It is rare that we can pick up a man who is able to see the chance, abnormal happening, which is very often the all-important and valuable thing. There is a gross error in loving the details of laboratory work—equally an error in being too accurate. It is of the greatest importance to thoroughly canvass a proposed piece of research work and to decide pretty clearly on how accurately the various parts of the work should be carried on in order to keep the whole thing within bounds. I once had an assistant who could not be taught to stop weighing everything that he weighed out to the tenth of a milligram, even though the nearest ten milligrams was abundantly close.

One of the large efforts of laboratory work has become what is known as life-testing, and where the life of the object is short enough to allow a natural life test to be made, little need be said on the subject, as it is perfectly straight-forward. Unfortunately, most objects last much too long for a genuine life test to be made, and much ingenuity is brought to play in the discovery of accelerated tests. We are now beginning to see in a number of different lines how we have been incorrectly guided by the tests based on assumptions that the chosen accelerated tests were actually the equivalent of life tests. The decision as to the minute details of the life test, and whether it is really representative should take the joint counsel and experience of everybody connected with the work, particularly outside men, salesmen and users, who will bring information to the laboratory which would never have been excogitated there.

I cannot close with stronger words than those of Professor Harper of Columbia: "Stimulation, initiation, regulation and coordination do not furnish motive power. They imply indeed an exhaustion of native energy, rather than its increase. The withdrawal of a man from the active pursuit of his own investigations for the controlling and direction of the research of others may be a deplorable thing. Routine solutions of definite and simple problems can be achieved by a factory-like system, but the highest achievements are always individual. In my opinion the distinction between routine research on problems already clearly stated

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and for which methods of attack are obvious and studies which really open up new fields is world wide.

"I think we must admit that many of the great advances in knowledge have been made by someone's breaking over the bounds of the average scientist's thinking and experimenting and attacking some problem which had been unthought of or else regarded so unclearly as to be considered visionary or ridiculous. The final success of the Wrights illustrates the weakness likely to inhere in governmentally supported research. Langley was unable to push farther his partial success to final achievement, while the Wrights could take their long chance without official explanation for repeated failures.

"It is the despair of organizations of research, that work of the first rank shows so little dependence on facilities and equipment.

"If we require for every research project that it appears promising and workable within a so-called reasonable time, we put a premium on problems of the easy and less fundamental type. As in so many socializing schemes, we put a premium on mediocrity and penalize real originality. Not by preaching research or organizing research but by feeling a deep and insatiable curiosity shall we advance."

THE DETERMINATION OF MOISTURE IN LEATHER.* 1920 COMMITTEE REPORT.

By Robert Wright, Chairman.

The Committee consisted of the following:

F. F. Marshall, Kistler Leather Company, Lock Haven, Pa.
P. T. Tarnoski, Chemical & Engineering Co., Chicago, Ill.
F. P. Veitch, Assisted by Ralph W. Frey, Leather & Paper Laboratory, Bureau of Chemistry, Washington, D. C.
Robert Wright, Reed Laboratories, New York.

The committee work was undertaken with the idea of finding out whether or no the present official method for moisture in leather gives correct results. It is necessary in analysing leather to obtain a fine preparation. This is done by means of circular saws and there is always some loss in the moisture content of the

* Read at the annual meeting of the A. L. C. A. at Atlantic City, May 28, 1920.

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leather. For many purposes this loss is not important as the analyses are calculated to some chosen moisture basis, but where the original moisture is desired, it is necessary to cut the leather by means of a plane or a sharp knife into small pieces. The question is as to how small these pieces can be and still dry properly. The members were instructed as follows:

Take a sample of sole leather marked into 3/16 inch squares and cut with a sharp knife. Immediately weigh off 10 grams of the preparation and dry for 16 hours in a combined evaporator and dryer, (such as is used in drying tannin residues.) Weigh quickly after dessicating over fresh sulphuric acid. These precautions are necessary, as dry leather absorbs moisture with great rapidity. Repeat the moisture determinations on the same samples, using 1/8 inch squares weighing off same as soon as prepared. Repeat using leather 1/16 inch thick which has been prepared by means of a carpenter plane. Repeat with planed leather 1/32 of an inch in thickness. All work on the sample should be done at the same time, thus preventing a change in the moisture of the same. Make similar determinations on a piece of heavily greased harness leather and also on belting leather.

This work was done on samples of leather obtained by the collaborators in order that the work might cover as great a variation in leather as possible. The results of these determinations were as follows:

	Sole leather Per cent. moisture	Heavily greased harness leather Per cent. moisture	Belting leather Per cent moisture
		VEITCH & FREY	
3/16 inch squares	8.73	9.00	9.33
1/8 " "	8.56	9.00	9.26
1/16 " planed sample	8.03	8.66	9.05
1/32 " planed sample	8.51	8.67	8.80
		MARSHALL	
3/16 inch squares	10.01	9.06	8.50
1/8 " "	10.05	9.17	8.79
1/16 " planed sample	10.05	9.22	8.75
1/32 " planed sample	10.14	9.18	8.77
		WRIGHT	
3/16 inch squares	9.85	10.39*	11.34
1/8 " "	9.98	10.86	11.31
1/16 " planed sample	10.08	10.56	10.93
1/32 " planed sample	9.85	10.76	11.01

* Leather contained 26 per cent. grease.

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The tests made on drying different sized pieces of leather show that moisture is liable to be lost in preparing very small pieces. This depends more or less on the operator. Furthermore it shows that coarse particles dry properly. However, Wright's results indicate that in the case of heavily greased leather the preparation must not be too coarse.

Two samples were sent out. "A" was heavily greased harness leather and "B" a belting leather. These were prepared by grinding very finely with circular saws and after allowing to assume their normal moisture in the laboratory, were put into bottles and carefully sealed. Sample A was prepared from one piece of leather weighing about 100 grams and the same was true of B. For these reasons the moisture content of all the different portions sent out should have been the same for each leather. It was desired to find out how closely the members could check on the moisture determination and furthermore to find out the rate at which the leather loses its moisture in the combined evaporator and dryer, so as to ascertain the proper length of time necessary for drying. The members were instructed as follows:

Weigh out 5 gram samples of these two leathers and dry these portions for 4, 6, 8, 10 and 16 hours respectively (do not attempt to put back to dry after weighing but let the drying for the time specified be continuous in each case). Should the sample continue to lose weight after drying 10 hours make certain that the weight obtained after 16 hours drying is constant. The result on these two samples are given below.

Examining the results of the three members who used a combined evaporator and dryer, it will be seen that Marshall shows a gradual increase in moisture with an increase in time for both samples A & B. That Veitch & Frey show a decided drop for both samples for the 16 hours drying period, and that Wright drops over the 8 and 10 hour periods but gains for the 16 hour period in both cases. This similiarity between both determinations (each member dried both A & B at the same time in the same oven) indicates that the fluctuations were due to a loss or gain of moisture since it is not possible that both A & B should fluctuate in the same direction at the same time due to oxidation of oils. Either temperature changes or the fact that the moisture was not carried away from the leather may have been at fault.

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This latter point is emphasized by both Marshall and Tarnoski who state that the leather must be spread out to dry properly.

SAMPLE A.

Per cent. loss after drying	4 hrs.	6 hrs.	8 hrs.	10 hrs.	16 hrs.	20 hrs.	24 hrs.
Veitch and Frey	6.31	6.58	6.59[1]	6.67[2]	6.24	6.69[3]	6.89[4]
Marshall	6.34	6.51	6.63	6.66	6.72		
Tarnoski*	6.33	6.66	6.68	6.98	6.77		
Wright	5.47	5.85	5.78	5.66	6.08		

SAMPLE B.

Per cent. loss after drying	4 hrs.	6 hrs.	8 hrs.	10 hrs.	16 hrs.	20 hrs.	24 hrs.
Veitch and Frey	9.68	10.30	10.18[1]	10.18[2]	9.65	10.02[3]	10.05[4]
Marshall	9.87	10.16	10.15	10.31	10.28		
Tarnoski*	8.99	9.07	9.35	9.46	9.97		
Wright	8.73	8.97	8.86	8.32	8.88		

[1] Dried 6 hours, kept in dessicator over night,, and dried 2 hours longer before weighing.

[2] Dried 7 hours kept in dessicator over night, and dried 3 hours longer before weighing.

[3] Obtained by 4 hrs. additional drying of the charges used for 16 hours continuous drying.

[4] Obtained by 4 hours additional drying of the charges used for the figures obtained under ([3]).

* Determination made in a gas (Griswold Bolo) oven at 100° C.

COMMENTS.

F. F. MARSHALL: I am of the opinion that the combined evaporator and dryer gives satisfactory results for moisture in leather and consider the Committee report to confirm the same.

In regard to the size of the sample for moisture in leather, while my results indicated that the finer the samples are cut the higher the moisture, the total variance between all sizes was but slight and I believe that with careful handling any one of the given sizes—that is, 3/16, ⅛, 1/16 and 1/32 inch—will give satisfactory results for moisture.

In reply to a request for suggestions Marshall replied "that it has been the writer's experience that when determining moisture on finely sawed leather that if the same is tightly packed into a moisture dish that it will not thoroughly dry in the 16 hours time allowed for the same. We have found it necessary to place this fine leather very loosely in a dish when determining the moisture.

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P. T. TARNOSKI: The results reported by me were made in a gas oven, and the test was continuous, *i. e.*, the oven was kept at 100° C. for the full length of the test.

From the results obtained, it seems to me that by careful attention to details, as good results can be obtained in the ordinary type of gas oven as can be obtained in a combined evaporator and dryer. The difficulty being in maintaining a constant temperature with a gas oven. The oven we use is an extra large one, and is known as a Griswold Bolo Oven, which is heated by a small gas ring. The ventilation seems to be exceptionally good in this oven, as results made in it, and in an automatically controlled electric oven check very closely. The reason we used this oven was due to the fact that the electric oven would not hold the samples, and it was my aim to make the tests at the same time, rather than hold some over for another day when atmospheric conditions would be different. It may interest you to know that we weighed the samples out on four inch watch glasses, the idea being to have as thin a layer of the sample as possible to dry. Our experience being that there is quite a difference in results made in different types of dishes or boxes. Along this line, I might suggest that dishes for moisture tests should be standardized. The idea being to have the same depth of sample in each case, which is impossible unless this is done. Another contention which I hold is that the quicker the drying is accomplished, the better will be the results, as far as correctness is concerned. Just how this can be accomplished, is still to be worked out. During the past year we have been working on Cotton seed meal, the co-operative results of some eighty chemists have been tabulated, and it is interesting to note the difference in the moisture on the same samples. In some cases the results show a variation of two to three per cent. above and below what the accepted average shows. The moisture determination was the only one in which there was any discrepancy, the oil and ammonia figures were in some cases miraculously close.

The question of ventilation is one which should be studied more thoroughly in my opinion. I really believe that more errors are made through this one factor than through differences of temperature in different types of ovens.

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R. WRIGHT: I do not believe the present official method for moisture in leather, that is, drying at from 95° C. to 100° C. is suitable. While I did not take the temperature of the oven when the determinations were made subsequent tests indicated that it was more a question of ventilation than temperature, and while it might be possible to get correct results within these limits to do so would necessitate very careful work and possibly a specially designed drying oven. Drying in a vacuum or using a temperature of a few degrees over 100° C. would probably be more suitable for this determination.

ABSTRACTS.

Study of Nitrification of Leather and Oil Cake. R. GUILLIN, *Bul. Soc. Agr. France,* 1917, Dec., pp. 357-360, Fig. 1, through *Exp. Sta. Rec.,* 41, 517 (1919).—Comparative studies of the nitrification of dried blood, tanned leather, chrome leather, burnt leather, leather dissolved in sulphuric acid, and oil cake in a calcareous clay soil showed an increase in nitrate in all cases except where the chrome leather was used, in which case there was a marked decrease in nitrate.

Pot experiments with wheat in which chrome leather and dissolved leather were added showed that considering the weight of the crop obtained from the unfertilized soil as 100 the weight of crop where chrome leather was used was only 30, indicating an injurious effect of the chrome leather. The crop was increased to 115 where dissolved leather was used, showing that this has some fertilizing value.

It is concluded that chrome leather has no fertilizing value and that furthermore it is injurious to crops. Neither tanned or burnt leather are considered to have much fertilizing value, while the value of dissolved leather is considered to be relatively high. No marked difference was noted between dissolved leather in liquid or pasty conditions.

Agricultural Utilization of Tanning Wastes. By B. FALLOT, *Vie Agr. et Rurale,* 9 (1919). No. 36, pp. 180-182, through *Exp. Sta. Rec.,* 41, 724 (1919).—This is a brief discussion of tanning waste with reference to its fertilizing value.

Analyses show that average tanning waste contains important amounts of phosphoric acid, potash, and lime, and a certain amount of nitrogen. It is stated that the tannic acid present may be neutralized with lime or removed by treatment with a solution of iron sulphate.

Coloration of Animal Hides by Means of O-Vanillin and O-Protocatechuic Aldehyde and Tanning With Aldehyde. By O. GERNGROSS, *Z. angew. Chem.,* 33, pp. 136-138 (1920).—Decomposition products of proteins (glycylglycine ester and tyrosine ester) give the same colorations

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with Schiff's *o*-protocatechuic aldehyde base as those produced in hides by *o*-protocatechuic aldehyde and *o*-vanillin. Formaldehyde-tanned leather does not give the same colorations as ordinary leather with these reagents, but reacts like ordinary leather with a solution of sodium diazobenzene-sulphonate, giving a blood-red coloration. This indicates that the imino group of the iminazole ring of histidine in formaldehyde-tanned leather has not been replaced by formaldehyde, and that no envelopment of the fibres by polymeric compounds of formaldehyde has occurred. The tanning properties of *o*-protocatechuic aldehyde are due not to an aldehyde, but to a dihydroxy group.

J. S. C. I.

The Determination of Formaldehyde in Solution. By R. H. ROBINSON, *Chemist Analyst,* April, 1919, p. 21.—The official method for the determination of formaldehyde in formaldehyde solutions, as recommended and outlined in the *Journal of the A. O. A. C.*, No. 1, Vol. II., Part II., p. 17, has been found by the writer to give erroneous results. In all probability the causes therefore are owing to loss of formaldehyde by volatilisation when heated on the steam bath or to incomplete oxidation of the formaldehyde to formic acid in the time specified.

In order to avoid any possible error caused by heating or lack of time for complete oxidation, the reaction was allowed to proceed at room temperature during several hours. Numerous determinations indicate that accurate results may be obtained in the determination of formaldehyde by employing the following method:

Measure 25 cc. of N/1 sodium hydroxide into a 200 cc. Erlenmeyer flask, and add 50 cc. of hydrogen peroxide. Weigh out accurately 1.5 to 2.0 grms. of the formaldehyde solution under examination, and add by means of a pipette, allowing the point to reach nearly to the liquid in the flask. Set aside for several hours or, preferably, over night. Titrate the excess sodium hydroxide with N/1 acid, using purified litmus solution as an indicator. One cc. of N/1 sodium hydroxide is equivalent to 30.02 milligrams of formaldehyde.

It is important that sufficient hydrogen peroxide be used. If a larger amount of formaldehyde than recommended above is taken for the analysis, more peroxide must be used. If the hydrogen peroxide is acid, neutralize with sodium hydroxide using the litmus solution as indicator.

The Determination of Sulfate in Sulfonated Oils. By E. J. KERN, *J. I. & E. C.*, **12**, 785 (1920). The author finds that a 10 per cent. solution of mono-sodium phosphate will give a practically complete separation of oil from solution with a sulfonated oil without the addition of a solvent and will extract all of the free and none of the combined sulfate. The method recommended is as follows:—Weigh from 20 to 40 g. of oil into a separatory funnel, add 100 cc. of a 10 per cent. solution of mono-sodium phosphate, shake, allow the oil and solution to separate, draw off the major portion of solution, and filter free from any oil particles,

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acidify 50 cc. of the filtrate, and precipitate the sulfate with barium chloride. In calculating the per cent. of free sulfate in the original oil, make allowance for the dilution of the solution by the water of the oil.

The Tanning Industry in Spain. *Commerce Reports,* Aug. 6, 1920. The tanning industry of Spain is of some importance, although scattered among a large number of small tanneries operating very much in a rut and with small forces. In all Spain there is not a tannery that has a technical director or a chemist, and the old process of tanning skins for soles and kips is still practiced. Before the war there were about 1,500 plants, with a total of 100,000 workmen. Since the war, tanneries for chrome tanning, especially of goatskins, sheepskins, and calfskins (box calf), have multiplied, but they have not attained the standard of perfection set by the foreigner, as there are no modern plants supplied with all the modern machines.

During the war, machines were introduced. Before that time the machinery for the manufacture of sole leather consisted only of a cylinder to calender the leather. The rest of the labor was manual and routine. The use of drums developed only a little before and during the war. Prior to that period the effort to introduce and sell tanning machinery cost the best factories of North America and Germany a great deal.

For the most part tanning, in the case of sole leather is done by the drum process with the use of tanning extracts. However, the old process of tanning by means of bark and extracts in a pit is common. As a rule the tanning done quickly is badly done.

The Igualada section has the greatest number of tanneries—240 or more, all small. These manufacture sole leather only, and in an unscientific manner. Each one has from 5 to 20 workmen. The families of the workmen also work in the industry. The sole leather is tanned by the drum process with extract of quebracho and pine liquor and the addition only of roldo (a species of sumac) and a little oak bark. The only change the tanneries have made in their methods to hasten the process of tanning has been the introduction of the drum, which is now in common use, and the use of extracts.

The number of important tanneries in Spain is small considering the population, which is 20,000,000 or more. This is because there is no promotive effort made and because the managers of the plants do not care to spend money for technical reviews, for machines, or for buildings, in order to attain the standard set by foreign manufacturers.

The School of Tanning at Barcelona was founded by a small group of manufacturers of leather because they wished to secure free training in order to perfect their products. This school began operation under the patronage of the Diputación de Barcelona.

The school is now being supported by the Mancomunidad de Cataluña and the revenue which it derives from the sale of manufactured leathers and that secured from the measuring, shaving, polishing, and softening machines.

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About six or eight students enter the school each year. The course covers two years—a year of theory and chemical laboratory work and a year of practical manufacturing. Few graduate with a diploma, because they do no care to study all of the subjects, but only tanning. As a result they only receive a certificate stating that they attended the school. Each year two diplomas carrying the title of Director Técnico de Tenería are granted following an examination and the submission of plans for the construction of a tannery for sole leather or chrome leather, etc. The equivalent of an American high-school diploma is required for entrance to the school, and it is very difficult to find anyone who has this qualification, as most of the applicants are privately and poorly educated. As a rule the sons of tanners have no education and hardly know how to write in Castilian. It requires great patience to teach them the laws of chemistry as applied to tanning. They desire to do the practical work at once without a proper foundation.

Determination of the Permeability to Water of Sole Leather. By E. JALADE, *Le Cuir* IX, 69-72 and 296-300 (1920). Among the factors affecting the degree of resistance of sole leather to penetration by water may be mentioned the degree of tannage of the leather, the nature of the tanning materials employed, the use of oil upon the grain, the amount of mechanical distorting of the leather, and its firmness, thickness, and density. But the mere analysis of a leather will hardly give the information desired regarding permeability and it seems desirable that this determination should be made by some special test.

In 1891 Balland found that army leathers absorbed different amounts of water depending upon the closeness of the texture. He found samples that absorbed as much as 96.8 per cent. of their weight of water, but regarded with suspicion any absorbing more than 55 to 60 per cent. The specifications of the French commissariat, drawn up following his investigations, required that all leather be tested by soaking samples 5 cm. square in water and noting the increase in weight after 30 minutes and after 24 hours. Only the figures for 24 hours were final. In 1912 the limits set for the 24-hour soaking were for rolled butts 50 parts of absorbed water per 100 of leather calculated to 18 per cent. moisture and for necks 55 parts. But this test does not give the rate of absorption nor does it allow for loss of water-soluble matter.

It is simple enough to compare the rates of absorption of water by different leathers. Some take up water so quickly that they give off a spray of air bubbles, but such leathers usually absorb their full amounts quickly and take up no more on long standing. Few leathers ever exceed the limits set by the specifications of the commissariat. The best leathers absorb water very slowly.

Testing leather by soaking in water is not always reliable as a practical guide. Sole leather presents only its grain surface to the action of water, when worn. While walking, the sole undergoes bending, with alternate contractions and expansions which favor the penetration of

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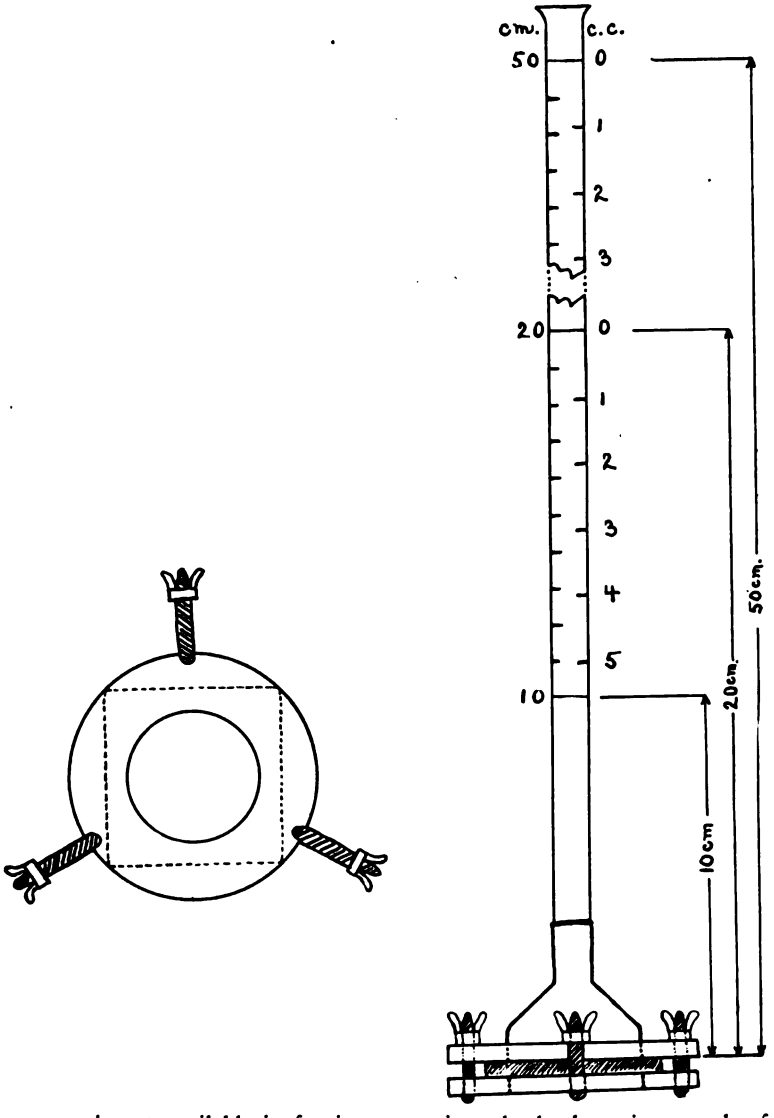
water. Furthermore, an average man's weight produces a pressure upon the soles of about 533 grams per sq. cm. or the equivalent of a column of water 533 cm. high. It must be recognized, however, that all of this



pressure is not available in forcing water into the leather, since much of the water is squeezed out from under the soles. These few considerations show how difficult it is to get a test corresponding with practical condi-

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tions. Nevertheless valuable comparisons are possible by studying leathers under fixed conditions and we have conceived the idea of measuring the quantity of water absorbed through the grain surface in measured time and under a pressure not exceeding 50 cm. of water.

In 1910 Thuau and de Korsak (This J. 5, 388) described a method for estimating the time required for 10 cc. water to filter through a leather with the aid of suction. Our objection to their method is that it is too drastic, the suction which they recommend causing a corresponding pressure greater than that of an average man upon the soles of his shoes, which we know is not all used in forcing water into the soles.

In 1916 Gayley (This J. 11, 36) did some work with a complicated apparatus in which an alarm indicated the time required for the passage of water through a leather under a pressure of about 60 cm. This method lacks sensitivity.

Jalade's apparatus is shown in Fig. 1. It consists of a glass tube of about 6 mm. diameter, graduated both as to height and volume, which is cemented to a metal part which holds the leather to be tested. The leather is held firmly between two nickeled copper plates, each 5 mm. thick and having a circular opening 36 mm. in diameter. The lower plate holds three screws capable of swinging into grooves in the rim of the upper plate. The wide rim of a metal funnel is soldered to the upper plate while the narrow end is cemented to the glass tube, as shown in the figure. When a piece of leather 5 cm. square is placed between the two plates and the screws are swung into place and tightened, no water can leak out from the tube above except by passing through the leather which exposes just 10 sq. cm. of surface to the water.

The glass tube is calibrated first as to height. A mark is made on the glass tube exactly 10 cm. above the lower surface of the upper metal plate. Calling this point the 10-cm. mark, the tube is marked off into tenths of a centimeter upward to the 50-cm. mark. This 50-cm. mark is then marked zero for the volume graduations, which are made to read downward and are found initially by running in water from an accurate burette. The 20-cm. mark is also taken as a zero-point in a set of volume graduations running downward. These two zero points were selected so that one might fill the tube to the higher point for very resistant leathers and to the lower one for leathers which absorb water readily.

After a square of leather has been put into place, grain side up, the measurement is made by inclining the tube and introducing the exact amount of water necessary to fill the tube either to the 20-cm. or the 50-cm. mark, as desired. The tube is then held upright and the volume of water absorbed can be followed by means of the volume graduations and should be noted at frequent intervals. A mirror is placed under the apparatus so that the flesh side of the leather can be more conveniently watched and the time is noted when water first appears on the leather as seen in the mirror. Given the weight of the 10 sq. cm. of leather exposed to water, it is a simple matter to calculate the grams of water absorbed

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per 100 grams of leather, since the volume graduations are also gram graduations for water. With this apparatus it is easy to follow the passage of the water through the leather and to compare the degrees of permeability of different leathers under rigidly fixed conditions.

The second part of the papers deals chiefly with a discussion of the "degree of tannage" of leathers because it plays an important part in the matter of permeability.

Without entering into a discussion of the theory of tanning, it may be admitted that tannin is present in leather in three states: merely present in soluble form between the fibers, coating the fibers as an insoluble deposit, and chemically combined with the hide fibers. The latter two forms are irreversible; together they are known as combined tannin and offer an explanation of the theory of tanning as well as furnish an important means of valuing leather. Von Schroeder gave the name "degree of tannage" to the number of grams of combined tannin per 100 parts of hide substance. For example, one leather showed by analysis:

Water	18.00	
Fat	0.21	30.13 non-leather
Mineral matter (insoluble?)	0.92	
Water-soluble matter	11.00	
Hide substance	40.00	69.87 leather
Combined tannin	29.87	
		100.00

The degree of tannage of this leather is therefore 29.87/0.4000 or 74.7.

So far as we know, the degree of tannage has not been the subject of very profound study and it is difficult to define the limits between which this figure may vary. Some chemists believe that hide cannot fix more than its own weight of tannin, or that the degree of tannage cannot exceed 100. But, since combined tannin is determined by difference, the degree of tannage is subject to the combined errors of several determinations and some indulgence must therefore be allowed in drawing conclusions.

In 1911 Appelius and Manstetten (This J. 6, 160) found that the degree of tannage is lower in the butt than in any other part of the hide, and notably higher in the flanks, which is easily explained by differences in texture and porosity. The neck proved to be more nearly representative of the whole hide than any other part. Differences were also found depending upon the time of tannage and upon the sex of the animal. The following figures show the extreme limits for the degree of tannage found in different parts of the same hide:

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After the second layaway:

Calf	from 85.6	to 98.8
Cow	94.0	to 101.0
Bull	87.1	to 93.8

After complete tannage in layaways:

Calf	from 94.9	to 110.7
Cow	85.6	to 97.5

After tanning in drum and washing:

Calf	from 92.2	to 111.5
Cow	92.1	to 98.1
Bull	93.5	to 96.0

They concluded that a hide has taken up its full amount of tannin the moment the tan liquor has completely penetrated it. In other words, they claim that the degree of tannage will not be modified by later tanning operations where the penetration has been complete in the handlers. They also claim a greater degree of tannage for hides tanned quickly in a drum with strong liquors than for hides tanned slowly in the ordinary layaways, which they attribute to the differences in concentration of the liquors. Their conclusions have not been confirmed and even appear to be contradicted by the work of others.

Riethof (This J. 14, 20) showed that hide absorbs tannin and combines with it to the end of the tannage. A hide which showed a degree of tannage of 90.3 after 142 days of tanning showed half of this figure in 27 days and four-fifths of it in 71 days.

The claim of Appelius and Manstetten that rapid tannages give a greater degree of tannage than slow ones is contrary to our experience. In Table I are given values for the degree of tannage of leathers obtained from tanneries all over France. These are divided into three groups, those obtained early in 1914 and tanned under normal conditions before the outbreak of war, those tanned after the requisition of the tanneries early in 1917, and those tanned in 1918 during the crisis in provisioning tanneries due to the curtailment of production and difficulties of transportation.

TABLE I.—Giving Values for Degree of Tannage of French Leathers.

Year	Method of tanning	Extreme values	No. below 50	No 50 to 60	No. 61 to 70	No. 71 to 80	No. above 80	Mean of 30 analysis
1914	slow	59–87	none	1	10	15	4	73.4
1914	medium	55–84	none	4	9	13	4	70.8
1914	rapid	50–90	none	9	16	4	1	64.0
1917	slow	56–79	none	7	11	12	none	67.0
1917	medium	47–76	2	7	13	8	none	63.8
1917	rapid	40–80	1	9	12	8	none	63.6
1918	slow	54–87	none	5	18	6	1	66.6
1918	medium	50–84	none	6	12	7	5	69.7
1918	rapid	50–83	none	13	12	4	1	63.3

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The figures in this table show that French leathers generally have a degree of tannage much lower than those mentioned by Appelius and Manstetten. Note that the values for slow and medium tannages have undergone considerable changes during the three-year period while those for rapid tannages have remained nearly constant. Contrary to the findings of Appelius and Manstetten, the rapid tannages show the lowest values for degree of tannage. The apparent high yield of rapid tannages is due to uncombined tannin, which will wash out and is therefore of little value to the wearer of the soles. The reason for the low degree of tannage of such leathers is that the strong liquors used frequently contain an insufficient amount of acid, and furthermore such strong liquors have a violent action upon the hide fibers, case-hardening them and thus diminishing their capacity for combining with tannin. Other factors, such as insufficient deliming, too little swelling, and improper graduation of the strengths of the liquors, also cause difficulties in tanning.

TABLE II.—SHOWING THE TIME REQUIRED FOR WATER, UNDER A COLUMN 20 CM. HIGH, TO PASS THROUGH DIFFERENT KINDS OF LEATHER.

Method of tanning	Degree of tannage	Time required for penetration	Remarks
Slow	73	22 hours	Heavy leather.
Medium	81	15 hours	
Medium	77	7 hours	
Slow	76	2 hours	Of foreign origin.
Medium	66	30 minutes	Of foreign origin.
Slow	56	30 minutes	Firm, slightly green.
Slow	56	10 minutes	Same leather as the one preceding, but after soaking in water 30 minutes and then drying.
Medium	90	25 minutes	Of foreign origin, washed.
Rapid	68	25 minutes	Of foreign origin.
Slow	88	20 minutes	Washed after tanning.
Medium	92	3 minutes	Washed after tanning.
Medium	62	3 minutes	Of foreign origin.
Slow	61	3 minutes	Insufficiently worked.

In Table II are given figures for the degree of permeability of leathers of different degrees of tannage. Where the degree of tannage is very low or very high, the leather is not very resistant to water. In the case of the more heavily tanned leather, the trouble is probably due to improper treatment during tanning. The most satisfactory resistance to water is shown by leathers with a degree of tannage lying between 70 and 80 and which have not been subjected to any unusual or drastic treatment.

The effect of washing leather after tanning will be discussed in a future paper. J. A. W.

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The Biology of the Warble and Means of Exterminating It. By CLEMENT VANEY, *Le Cuir* IX, 249-52 (1920). Warbles are most abundant from March to August, usually reaching a maximum about June or July. In the Lyonnaise region of France the number of warbled hides during 1909 reached a maximum in July of 14.53 per cent., while in 1908 the maximum occurred in June with 20.90 per cent. or more than one-fifth of all the hides. The warble is best studied in May or June and may be found in swellings near the backbone from which it is a simple matter to squeeze it out, at which time it is about 3 cm. long, with a wart-like surface and of a grayish color. It lives with its head plunged into pus and breathes through its posterior by means of two pores directed towards the opening. (This is shown in Fig. 1 which was taken from a review of Vaney's article in *Les Industries du Cuir* of June 20, 1920.) Living warble flies are found only from March to August. Those found in hides in winter are dead or the remains of warbles that did not develop.

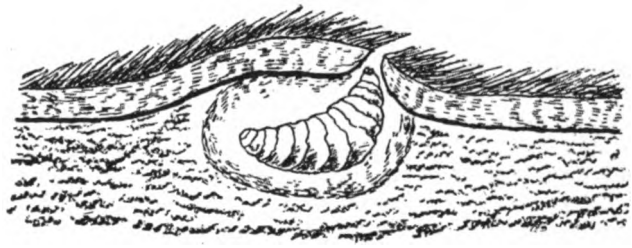

Fig. 1.

Opinions still differ as to the manner in which the warble makes its way under the hide. Stub maintains that the fly lays its eggs under the hide, but this is not possible, judging from the structure of the female; nor has anyone seen the flies on the backs of the animals. Moreover, the eggs have been found on the hair of the cattle. They are placed at the base of the hairs on the thigh or flanks, but never on the back. Nor does the larva itself penetrate directly; a larva put on the back of a calf does not penetrate, but remains indifferent. The author has never found young larvæ in the interior of the hide, but on the other hand he has found numbers of them in the esophagus. His theory is that the animals lick the eggs from their legs and lower regions and that the first stage of development of the larva is in the esophagus.

Young cattle are more likely to be infested than older ones. In one district 52 per cent. of the cattle from 1 to 2 years old were warbled against only 4 per cent. of the cattle over 3 years old. Cattle left in the pasture all night are more likely to be infested than those kept in stables. A warm summer favors the laying of eggs and their return the next year.

The warble not only damages the hide but causes digestive and nervous disorders in the cattle which prevent their proper development and lessen the value of the meat and milk.

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The author then discusses means of exterminating the pest. Trying to kill the flies is not effective because they are hard to find and are easily confused with other flies. Methods for preventing the laying of eggs have not been sufficiently developed. The destruction of the eggs is not practical because of their small size and the fact that they are covered with hair and difficult to reach. He recommends systematically squeezing the larvæ out from the swellings on the hides and destroying them. This would still leave holes in the hides, but if carried out generally, the pest would in time be exterminated. J. A. W.

A Critical Study of the Warble in Reply to the Incorrect Statements of C. Vaney. By H. PERICAUD, *Le Cuir* IX, 350-54 (1920). Pericaud takes issue with Vaney on nearly all of the latter's theories concerning the warble (see preceding abstract). Contrary to Vaney's assertions, the eggs are nearly always laid on the animals' backs, but rarely on the flanks. The eggs are usually fixed so firmly at the base of the hairs that the animal cannot remove them with its tongue. Pericaud recommends that Vaney spend several whole days in the pasture as he has done and really study the warble. The fly is easily distinguishable from other flies. The female hovers over the back of an animal for a moment and then swoops down rapidly and places an egg on the back. It flies up again quickly and then strikes again placing a second egg. This is continued until all its eggs have been placed. More eggs are placed on cattle under two years of age because of their more tender skin; the skin of an older animal is too tough to permit of easy penetration. Pericaud is convinced that the penetration of the skin by the warble is direct and not by way of the digestive tract, which is very rare. He also maintains that young warbles abound under the skins of the animals in winter. Finally he criticises Vaney's method of exterminating the warble by cutting it out and leaving a dangerous hole in the skin. He recommends treating the animals with an empyreumatical oil which is quite efficacious against the warble.

J. A. W.

The Preparation of Lightly Chromed Hide Powder for Tannin Analysis. By G. BALDRACCO and S. CAMILLA, *Le Cuir* IX, 152-4 (1920). The preparation of hide powder really suitable for tannin analysis presents such difficulties that it has been found necessary to appoint a special committee to control the "Standard" hide powder and furnish it in a proper condition for use. In spite of all precautions, however, complaints against the hide powder are occasionally heard and at the International Congress in Paris in September, 1919, claims were made that hide powder from the same lot was not always uniform.

Nevertheless it is quite natural to wonder if these complaints are justified and if it really is the hide powder which is at fault and not the method of analysis or the conditions under which the hide powder is used. The experience of the authors has been that the "Standard" hide powder gives results with the official method identical either with the

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Freiberg powder or that prepared under their own direction. On the other hand, it was found that for certain materials the official method is apt to give unreliable results, whereas accurate results are obtained under all conditions by the authors' modification of the official method in which a hide powder previously chromed and dried is used. (This J. 15, 201).

One disadvantage of the present official method lies in the washing of the chromed powder to insure that it gives off no soluble matter to increase the non-tannin figure, because there is washed out at the same time the acid which is necessary for the absorption of phlobaphenes by the powder. It was for this very reason that we decided to prepare our lightly chromed powder, which is of constant composition, contains no mineral matter capable of passing into solution, and requires no washing previous to use.

After some preliminary experiments in making this hide powder, we adopted the following procedure. After soaking, the hides are fleshed, trimmed, and washed and are then kept for 24 hours in a dilute solution of ammonia (10 cc. of ammonia, of gravity of 0.91, per liter). The hides are then washed and the hair is shaved off with a razor of the Gillette type. They are washed again, allowed to drain, and are then dried at room temperature. The dried hide is then ground to powder in a suitable grinder and is then in a condition for use by the official method, but must be subjected to a chroming process for use with the authors' modified method. The hide powder is thoroughly soaked in water and for each 100 grams of dry hide powder 2 grams of chromic chloride dissolved in a convenient quantity of water are added and the whole is shaken for 15 minutes. The chrome solution is purposely not made basic so that the powder will retain the acid from the solution. The wet powder is dumped into a cloth and the water squeezed out by means of a screw press. After drying in a current of air, the powder is again ground up in the grinder and is then ready for use with the modified method of tannin analysis.

It is hoped that an international committee will be appointed to take up the study of this hide powder as well as of the authors' proposed modifications of the official method of tannin analysis. J. A. W.

A Modified Shake Method for the Analysis of Tanning Materials. By G. BALDRACCO and S. CAMILLA, *Le Cuir* IX, 257-63 (1920). *J. S. L. T. C.* IV, 101-111 (1920). Some time ago the authors proposed a modification of the Official Method of tannin analysis of the Society of Leather Trades' Chemists (complete translation, This J. 15, 201-212). The modifications were suggested primarily to make the Official Method easier of execution, but they now find that their Modified Method is not subject to a grave error which occurs with some extracts, when using the Official Method. This error arises from the prescribed method of preparing the hide powder. The washing of the powder, after chroming, actually removes acid which is necessary for complete combination between hide powder and tannin. The lightly chromed hide powders as prepared

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for use with the Modified Method (see precediing abstract) always contains sufficient acid to enable it to combine with all the tannin.

While comparing the non-tannin filtrates obtained from the same extracts by the two methods in question, they sometimes found that the filtrates from the Official Method were distinctly colored, while those from the Modified Method were colorless. But the gelatin-salt test gave negative tests for both sets of filtrates. Guided by some of Camilla's earlier work, they came to the conclusion that the gelatin-salt test is sensitive only for liquors that are distinctly acid. They therefore devised a new reagent consisting of gelatin and acetic acid and this gave distinct tests for the colored non-tannin filtrates of the Official Method, but none for the colorless filtrates of the Modified Method.

The gelatin-acetic acid reagent is made by dissolving 0.9 gram of high grade gelatin in 50 cc. water, with warming, and then adding 10 cc. glacial acetic acid. It is then filtered and is ready for use. It is claimed that this reagent is capable of detecting one part of tannin in 150,000, if used when freshly prepared, and in the quantity of one drop to each 4 or 5 cc. of solution.

The figures in Table I show how the value for non-tannin is increased in the Official Method through failure of the hide powder to combine with all of the tannin.

TABLE I.

	Per cent. of non-tannin	
	Official method	Modified method
Liquid Chestnut Extract	12.85	10.91
Liquid Chestnut Extract	12.67	10.74
Liquid Mimosa Extract	11.00	9.44
Natural Chestnut Extract @ 26.2 Be.	13.93	13.28
Decolorized " " @ 29.5 Be.	13.70	12.90
Natural tan liquor @ 3.6 Be.....	6.00	5.80
Decolorized tan liquor @ 3.6 Be. ..	2.52	2.66
Chestnut Bark	3.45	2.88
Pine Bark	13.56	13.55

Where appreciable differences between the two methods were found, the non-tannin filtrate from the Official Method was colored. Where the results were nearly the same, the filtrates from both methods were colorless. The non-tannin filtrates from the Modified Method were colorless in all cases. J. A. W.

A Criticism of Baldracco and Camilla's Modification of the Official Method. By E. SCHELL, *Le Cuir* IX, 327-28 (1920). (See preceding abstract.) When comparing any method of tannin analysis, it is essential that the nature of the particular lot of hide powder be taken into con-

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sideration. Recent lots of hide powder showed two whole units more absorption of non-tannin from chestnut extract than previous lots of hide powder. Under the conditions prescribed by the Official Method, the gelatin-salt test is quite sensitive enough. Detannization of a liquor is never absolutely complete, but in the Official Method the amount of tannin left in solution is so small as to be negligible so far as practical results are concerned. On the other hand, attempts to remove the last traces of tannin increase the amounts of non-tannin absorbed. Absence of tannin in the non-tannin filtrate is not the only criterion of the value of a method; it is equally important that no non-tannin appear as tannin. Baldracco and Camilla's method is not as exact as the official method and the hide powder they propose is not as well defined as the official hide powder. Moreover their tannin figure includes more non-tannin than is the case with the official method. To abandon the rigid requirements of the Official Method would be a step backwards. J. A. W.

Mimosa Bark and Extract. By "NATAL," *Lea. World,* July 15, 1920. The author claims that one of the main reasons why mimosa is becoming one of the most popular of tanning materials is due to the fact that its composition is remarkably constant. This is shown by the following analyses of four recent deliveries of solid extract.

Tannin, per cent.....	60.5	62.0	62.6	63.4
Non-tannin, per cent....	17.9	19.0	18.8	18.0
Insoluble, per cent.....	4.8	2.1	1.9	2.2
Moisture, per cent.....	17.5	16.9	16.7	16.4
Red	4.9	3.7	3.4	3.6
Yellow	7.0	4.1	4.0	4.0

The last three extracts are from the same factory. The method of extraction employed by the producer of the first extract differs from that of the producer of the last three. Research work is continually being done with the object of improving the leaching process and thereby the quality of the extract.

Realizing the importance of maintaining a regular grading of wattle bark, the Government of the Union of South Africa in 1914 instituted a series of grades as follows:

H.1 Heavy (choice)
H.2 Heavy (fair average quality)
M.1 Medium (choice)
M.2 Medium (fair average quality)
T.1 Thin (choice)
T.2 Thin (fair average quality)
B.G. Below grade.

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In the inspection, at least 10 per cent. of the bags to be exported are examined by the official examiner, who, on finding them up to the standard claimed, issues a certificate to that effect.

Cultivation of the wattle in South Africa has met with many difficulties. Disease is by no means unknown and research has been done with the object of combating any outbreaks. G. W. S.

Soaking of Hides and Skins. *Gerbereitechn. Auskunftsb. fur die Gesamte Lederind,* through *Gerber-Courier,* June 19, 1920. The object of soaking is to cleanse the hide and at the same time to change it from the dry state to that of maximum swelling. With green hides it is simply a matter of cleansing which can be accomplished quickly; longer soaking will only do harm. With running water 2 to 3 hours is sufficient, otherwise about 12 hours providing the water is pure. With green salted goods it is necessary to remove the salt to bring the hides back to their original swollen condition. The salt can be extracted quickly in running water. In soaking vats or paddle vats, with fresh water entering from above and the dirty water flowing from the bottom this can be accomplished in the shortest time. Cow and steer hides require a three to four day soak when the water is changed each day and then finally drummed for ten to twenty minutes in running water. The most suitable method for dry hides is soaking in water for two or three days until they can be milled, then soaked again in fresh water and placed in the limes while fairly tough. If the hides receive suitable treatment from here on they will yield a good, plump leather. Dry hides, like E. I. kips, flint hides from Texas, South and Central America are soaked longer the more they are dried out. Dry salted hides soften somewhat easier. For soaks the most suitable is pure water free from organisms—it should not be running but well water and the well should be at least five meters deep.

The main point in soaking is to see that the hides do not putrify. Soaking should not last longer than three or four days, this period is sufficient for all kinds of hides and a longer period is only futile. The action of the soak can be accelerated by mechanical aid and by the so called "sharpeners." The hide mill is usually employed after the hides have been soaked for a time when they are returned to the soaks. It is necessary to see that the hides come to the mill sufficiently softened so that the hide fibers will not be broken or the grain damaged. Calf and goat hides are not milled but when necessary they are worked on the grain side with a blunt breaking iron. The mechanical working of the hides is omitted when the soaks are sharpened. Sodium sulphide is frequently used for this purpose. Caustic soda is considered better, especially for hides and skins having a high fat content. Procter recommends the use of sulphurous acid which gives a good effect in weak solutions.

If the soak is sharpened, then, as a rule, sharpening of the limes is omitted for heavy leathers. On the other hand it has proven useful to sharpen both for many fine and upper leathers. G. W. S.

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PATENTS.

Tanning. British Patent 140,092. TANNAGE RATIONNEL MEURANT, SOC. ANON., Liege, Belgium. March 10, 1920. To accelerate tanning processes, compressed or liquid air, or oxygen in a more or less compressed state is brought into contact with the hides. The hides to be tanned are placed in closed pits into which there is admitted either pure water or water containing tanning substances and air or oxygen compressed more or less strongly according to the nature of the hides. The closed pits containing the hides may be supplied from a central pit, the liquid being in constant circulation and, if necessary, filtered on leaving the central pit.

Lignone Compounds; Tanning-Agents. British Patent 140,359. PAPETERIES BERGES, SOC. ANON., Lancey, Isère, France. July 7, 1919. Halogenated lignone compounds and the like are obtained by treating with halogen or halogenating-agents, particularly chlorine, the waste liquors from the manufacture of paper by treating wood with bisulphites, alkalis, steam etc., or waste liquors obtained in the retting of flax or other vegetable fibres. The waste liquors may be acidified and treated with steam before the treatment with halogen. In the case of bisulphite waste liquors, they may be given a preliminary treatment with alkalis or alkaline earths under pressure. The products can be obtained as extracts, pastes, or dried powders, and may be used in tanning.

Artificial Leather. British Patent 141,385. MILLER, G., Meopham, Kent. July 3, 1916. Artificial leather is made from paper, alone or combined with a textile fabric, by treating with a vegetable glue such as is obtained from bananas, or from the farina of *colocasia esculadium,* mixed with water containing 2-5 per cent. of glycerine, with or without the addition of isinglass, casein, gum damar, or other agglutinant. The material is then air-dried and may be dyed. The material so treated may be waterproofed with a mixture containing a vegetable wax such as carnauba, mixed, for example, with paraffin wax and turpentine. A number of sheets may be superposed, and the material may be finished to give it the appearance of ordinary leather.

Synthetic Tanning Agents. British Patent 141,714. ROHM & HAAS CO., 40 North Front Street, Philadelphia, U. S. A. (Assignees of *Koetzle, A.*) *Methylenesulphosalicylic acid compounds.*—A tanning-agent is prepared by condensing *p*-sulphosalicylic acid with formaldehyde. The process may be carried out by dissolving *p*-sulphosalicylic acid in concentrated sulphuric acid, adding formaldehyde and stirring for several hours, and finally diluting and neutralizing the sulphuric acid with alkali.

Art of Tanning. U. S. Patent 1,338,307. C. KROUSE, Williamsport, Pa. Filed June 20, 1919. The herein described method of treating raw hides and skins, containing a high percentage of fat, preparatory to tan-

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ning, consisting in adding to the hides and skins sufficient quantity of grease solvent to dissolve the grease so that when the solvent is withdrawn it carries enough of the grease with it to bring the skins into a condition for tanning to produce strong leather, substantially as described.

Degreasing Apparatus. U. S. Patent 1,338,308. C. KROUSE, Williamsport, Pa. Filed Jan. 27, 1920. Apparatus for degreasing hides and skins comprising a closed solution tank having a closure at one side, parallel hollow spaced heating elements located in said tank with means for supplying heating fluid thereto, guides arranged between said heating elements, reticulated supporting frames for the hides and skins to which said hides and skins are clamped, liquid supply and withdrawal means connected with said tank, and vacuum producing means connected with said tank.

Hide-Stretcher. U. S. Patent 1,339,093. ALEXANDER BERG, St. Louis, Mo. Filed June 27, 1919.

Manufacture of Mocha Leather. U. S. Patent 1,339,751. LYNDALL FORSE, Yeovil, England. Filed Dec. 29, 1916. The method of manufacture of Mocha leather characterized by applying on one side only of a skin a solution of an agent adapted to attack the skin, thereupon completely removing the whole granular surface of the skin, thereby producing a leather which is soft and velvety throughout.

Leather-Working Machine. U. S. Patent 1,340,262. FRANK W. TUCKER, Lynn, Mass. Filed Sept. 3, 1918. Serial No. 252,351.

Leather-Working Machine. U. S. Patent 1,344,467. ROBERT F. WHITNEY, Winchester, Mass. Filed April 19, 1919. Serial No. 291,242.

Tanning Material and Method of Producing the Same. U. S. Patent 1,344,951. ARTHUR KOETZLE, New York, N. Y., assignor to Rohm & Haas Company. Filed April 12, 1919. A tanning material comprising the condensation product of a sulfo-phenol-carboxylic acid with formaldehyde, which product is amorphous, soluble in water and produces a leather which is substantially colorless, strong and pliable.

Tanning Material and Method of Producing the Same. U. S. Patent 1,344,951. ARTHUR KOETZLE, New York, N. Y., assignor to Rohm & Haas Company. Filed June 6, 1919. A tanning material comprising a condensation product of a sulfo-cresol carboxylic acid with formaldehyde which product is amorphous, soluble in water, adapted to precipitate glue and gelatin in acid solutions and which produces a substantially white, soft and strong leather.

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CONTENTS

Elections - - - - - - - - - 551
Second Meeting of the Section of Leather Chemistry of the American Chemical Society - - - - - - - 552
Some Considerations on the Testing of Dyes in the Leather Industry. By Louis Joseph Matos - - - - - - - 553
On the Swelling and Falling of White Hide in Vegetable Tan Liquors. By George D. McLaughlin and Ralph E. Porter - - - 557
The Determination of Water Soluble in Leather. 1920 Committee Report. By G. L. Terrasse, Chairman, and J. F. Anthes - - - 581
Order of Diffusion of Tanning Extracts through Gelatin Jelly and Their Relation to Results Obtained by Wilson and Kern. By Arthur W. Thomas 593
The Analysis of Sulphonated Oils. - - - - - 595
Abstracts - - - - - - - - - 599

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SECOND MEETING OF THE SECTION OF LEATHER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY.

In connection with the sixtieth meeting of the American Chemical Society, the Section of Leather Chemistry held its second meeting on September 8th and 9th, at Chicago, Dr. A. W. Thomas presiding. The program was as follows:

Nature of the Hide—Tannin Compound and its Bearing upon Tannin Analysis by John Arthur Wilson and Erwin J. Kern.

The Mechanism of Bating by John Arthur Wilson.

An address by Dr. Roberts of the Du Pont Co., on the necessity for analyzing all dyestuffs used in the tannery.

An account by Victor Kadish of a method for recovering fertilizer material from waste sulphide liquors.

A paper by George D. McLaughlin and R. E. Porter dealing with the swelling and depletion of hides in tan liquors to which have been added various amounts and proportions of certain organic acids and salts.

A paper by A. C. Orthmann on the general scheme of management of the laboratories of the Pfister & Vogel Leather Co.

A paper by Alan A. Claflin on experimental results dealing with the effect of acids in precipitating the constituents of vegetable tan liquors.

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A paper by Arthur W. Thomas and Margaret W. Kelly dealing with various phases of chrome tanning.

A paper by Arthur W. Thomas and A. Frieden on the estimation of hydrochloric acid in leather.

The last paper, by Professor Thomas, dealt with the rate of diffusion of tan liquors into gelatin jellies.

The next meeting is to be held in New York City with the Society next September. The new officers of the section are: John Arthur Wilson, Chairman, and George D. McLaughlin, Secretary.

SOME CONSIDERATIONS ON THE TESTING OF DYES IN THE LEATHER INDUSTRY.*

By Louis Joseph Matos.

Upon receiving from your President the invitation to be here to-day it occurred to me that a few comments might not be out of place on some phases of dye testing as applied to laboratory work on leather which without doubt has received attention at your meetings from time to time. You are not unaware of the fact that the testing of dyestuffs upon leather is one of the most unsatisfactory problems that either a leather man or a colorist has to contend with. The testing of dyes from the leather trade standpoint brings two points to mind:

(1) The testing of dyes for the purpose of ascertaining the properties of the dyes, the colors and shades they are capable of producing, together with their working qualities.

(2) The other feature is more of a practical character insofar as it relates to the tannery, and has to do with the proper use of coal tar dyes upon various tannages. In this latter case, it is not so much what the dye is capable of doing, but what opportunity the leather under consideration can be made to look like by using dyes.

Two classes of leather are generally made use of in the laboratory—chrome tanned stock and vegetable tanned stock. One point having to do with both of these tannages is the necessity that devolves upon the colorist to make sure that the leather he is

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using for the test sample is practically clean and particularly free from grease.

Speaking particularly of chrome leather that is to be colored with dyes of coal tar origin, it is necessary that the samples be well neutralized with alkali in order to insure the complete removal of any traces of acid that remain in the skins, and, further, after this acid removal has been effected, that the alkali used for the purpose should in turn be thoroughly removed by washing. The presence of acid, or its absence, should be positively determined by the proper use of test paper and that the removal of acid should be done by means of borax. If traces of alkali are present their complete removal should be effected by thoroughly washing the pieces with luke warm water until neutral, and the neutrality assured by means of test paper again. It is a fact that many so called off-shades appearing on test samples can be traced directly to the presence of either acid or alkali. This is particularly noticeable when test samples of leather colored with various dyestuffs in the laboratory are compared with clippings of hides that have been colored in the drum. Marked differences that have appeared from time to time have been attributed to one cause or another, but it is generally found to be true that the differences in shade are the result of either imperfect neutralization of acid or alkali.

Another point that should not be overlooked in connection with the foregoing is the age of the leather employed in making the tests. It is well known to you all that chrome tanned leather which has been kept for an indefinite length of time after tanning seems to lose to a considerable extent the property of taking up coloring matters from the dye bath, and hence some dyestuffs have been said to be tinctorily weak when tested on such skins. When skins have been tanned and passed directly from the tanning through the wash and then into the dye bath they are in a prime condition to take up the color, and hence deeper shades appear upon such skins with a given dye than when the same dye has been applied to chrome tanned test pieces that have been out of the tan liquor for several weeks. It is desirable in this connection to emphasize the necessity of standardizing, if possible, the methods for testing coloring matters upon leather. To adopt a method for such work requires that there should be a unanimity

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of opinion based upon laboratory trials extending for a reasonable length of time and which have been made by leather colorists whose views in the matter might be collected and a method evolved. Such is desirable, not only from the leather man's standpoint but also from the standpoint of the dye maker.

Dyeing of chrome tanned stock with the basic dyes requires that the sample should be first treated with sumac or gambier, then fix with either tarter emetic or potassium titanium oxalate followed by thorough washing. This washing appears to be particularly necessary to avoid the possibility of titanium lakes forming with the dye base in the skin. In this connection it would seem proper that some opinion be given as to the quality of either the sumac or gambier made use of. It has been noticed from time to time in comparing laboratory test samples of such chromed tanned stock that the quality of the vegetable tanning matters used has had a marked influence upon the clarity of the shade shown by the test. In dyeing test samples with the acid colors the necessity for chemically neutralizing and cleaning skins is again apparent, notwithstanding the use of acid in the dye bath.

A desirable procedure appears to be to stuff the test sample with as much dye liquor as possible before adding any acid to the dye bath. Here the procedure is based upon that commonly employed in dyeing wool—the addition of acid to a dye bath at the same time that the dye has been added seems to cause many quick dyeing acid colors to go on either wool or leather so rapidly that uneven shades result. Sometime this unevenness of the finished dyeings on leather has been directly attributed, however, to the difficulty above mentioned; while, upon investigation in the laboratory it has been found that the unevenness has been due to traces of grease that were not properly washed out in the preparatory operations.

The writer recalls an incident that occurred in a tannery where trials upon a practical scale were being conducted upon calf skins. A number of the skins when finished were irregular in appearance, even mottled, and it seemed as if the color had "jumped on" from the dye bath. Upon cutting out some of the darker portions and extracting them with ether, it was found that noticeable traces of grease were present and that when the same extracted samples had been dried, the shade was normal. In dyeing test samples

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the purpose of the colorist should be to imitate as closely as possible the operations of drum dyeing. This may not always be possible, but a very good approximation, so far as results are concerned, may be secured by using glass containers of a sufficient size to permit a certain *throw* or *impact* of the test sample in and with the dye liquor.

For this purpose it is recommended that long cylindrical glass jars be used. Such jars are sometimes found in museums. They are about 12 inches in length and 3 inches in diameter, and may be operated by hand, which I admit is rather a tedious operation on the part of the operator, or they can be mounted on a shaker of some sort. Such a shaker may be made of a tilting board or box mounted on a fulcrum connecting with an eccentric, a row of such bottles laid parallel to each other can be clamped to the top of the board and the oscillating motion imparted to it in a direction parallel with the length of the bottles.

Regarding vegetable tanned skins, their treatment is of the greatest importance. As a rule, only a single skin finds its way into the laboratory, which, owing to the high price of leather is all that could be permitted; while, on the other hand, clippings of skins, mostly from the shanks are given to the colorist, but it seems that the latter are the less desirable inasmuch as they usually have quantities of grease in excess of that found in other parts of the hide. Greasy skins are known to cause the greatest amount of trouble in color work and should receive very careful attention. The most important operation being to wash the skins or samples in fair quantities of warm water heated to about 100° F., and the amount of time required to make the test should be perhaps one hour, although the experience of the operator will decide whether an hour is sufficient. No doubt, some skins may be sufficiently freed from grease in three quarters of an hour, but an hour appears to be a fair average.

Simply agitating the skins from time to time in luke warm water has not been found to be sufficient. There must be an agitation that includes the impact of the samples or skins against each other and against the ends of the vessel in which the cleansing takes place. By the impact, the traces of grease in the presence of warm water emulsify and in time are loosened and removed.

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As to the size of test samples, opinion, no doubt, will vary, but it seems where possible that pieces 6 inches square are desirable since when such pieces are dried and finished they will show a fair surface and the operator can with greater safety judge the value of the dye, or the adaptability of the leather to the dye. Pieces 3 x 6 inches may also be used. In careful tests the writer suggests that even larger vessels be used permitting the introduction of several 6 x 6 inches, or a corresponding number of 3 x 6 inch pieces, these pieces to be taken from different parts of the hides.

Owing to the use of many dyes that are mixtures, due regard must be given to the fact that some of the dyes may be taken up more rapidly from the bath than others and unless a sufficient amount of time is given for the test, errors of judgment may result as to the value of a dye. It, therefore, becomes necessary in making tests of mixtures that preliminary tests with the individual components of the mix be made before hand. Where mixtures of acid and direct dyes are used, due regard must be paid to the possibility of some of the direct dyes changing their tone under the influence of mineral acids and here again the necessity is made prominent of thoroughly washing the skins with borax, then with ammonia, followed by a luke warm drench to insure their neutrality before going into the dye bath.

ON THE SWELLING AND FALLING OF WHITE HIDE IN VEGETABLE TAN LIQUORS.

By George D. McLaughlin and Ralph E. Porter.

Received August 23, 1920.

When a sample of tanning material or tannery liquor is analyzed by the Official Method, the analysis yields certain empirical results. These results serve as the basis for the sale of the tanning material, or to indicate whether the given tan liquor differs in its empirical constitution from previous analyses of the same liquor. The analysis *does not* state the value of either of the two samples in respect to their character of tannin, whether the system would be termed "mellow" or "astringent;" nor does it give any information as to the swelling or depleting power of the various organic or inorganic constituents. The net result of such conditions is that the practical tanner is forced to lean more heavily

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upon observation and experience than upon his scientific colleague. Our own conception of the cause of such a condition is: that chemists have paid too much attention to routine and too little to research in fundamentals.

We purpose here showing, first; some of the actions of each of the main ingredients of some vegetable tanning materials upon white hide; second, their inter-relation; and third, we will outline the methods which we recommend for a broader assay of tanning materials and conditions.

Throughout all the experiments hereinafter described we have employed limed and hydrated steer hide, as it leaves beam house. Cutting our specimens from along the back edge of side, starting from about three inches above the tail root and extending eighteen inches beyond and six inches in, we secure a rectangle of hide showing markedly uniform structure and hydration throughout. Exactly thirty grams of such hide are immersed in two hundred and fifty cc. of solution under examination for twenty-four hours. In choosing a twenty-four hour period of immersion we have in mind the necessity of adopting some definite period. Extension of immersion to forty-eight hours, for example may change results slightly in specific instances. This, however, is a relative matter, the important point being the use of the same time period throughout any given set of experiments. (NOTE: the vessel used must be of such shape that the hide will stand in a slanting position, touching the vessel at its edges only; this allows a uniform circulation of the solution. Should the hide lie flat the experiment is useless. We have found pint glass fruit jars quite satisfactory vessels.) Prior to each weighing the hide is *gently* pressed between filter paper, so that all excess surface liquid is removed. Weighings must be made on a sensitive balance. After a reasonable amount of practice in the technique described, one may secure remarkably concordant results, varying not more than ½ per cent.

It will be immediately recognized that such a method starts with the actual materials and conditions which exist in the tan yard. We thus eliminate the otherwise necessary assumptions as to the relation between some other material which might be employed for such tests — such as gelatin or hide powder — and the white hide of the tannery.

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Selecting a certain tail rocker liquor, for example, we found it to contain, by the Official Method:

Per cent.	
2.60	Total Solids
2.00	Non Tannin
.50	Tannin
.25	Acid (as Acetic)

The sample also contained 14 per cent. ash, calculated on its total solids. This liquor caused white hide to lose 3 per cent. of its weight after twenty-four hours immersion. *Why?*

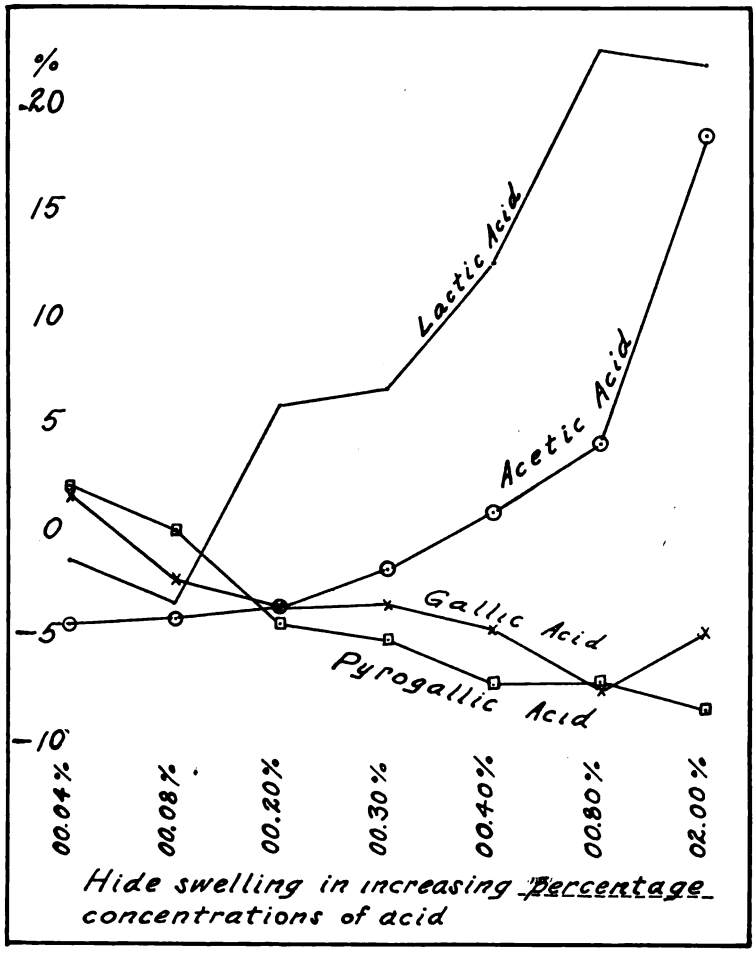

Fig. 1.

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The sample described contained lactic, acetic, gallic and pyrogallic acids. If we soak white hide in aqueous solution of each of these acids, we find the following weight gains and losses:

TABLE I.

Concentration	Lactic Per cent.	Acetic Per cent.	Gallic Per cent.	Pyrogallic Per cent.
00.04	—1.0	—4.0	+2.0	+2.3
00.08	—3.0	—3.7	—2.0	+0.3
00.20	+6.3	—3.3	—3.3	—4.0
00.30	+7.0	—1.3	—3.0	—4.7
00.40	+13.0	+1.3	—4.3	—6.7
00.80	+23.0	+4.5	—7.0	—6.7
02.00	+22.3	+19.0	—4.3	—8.0

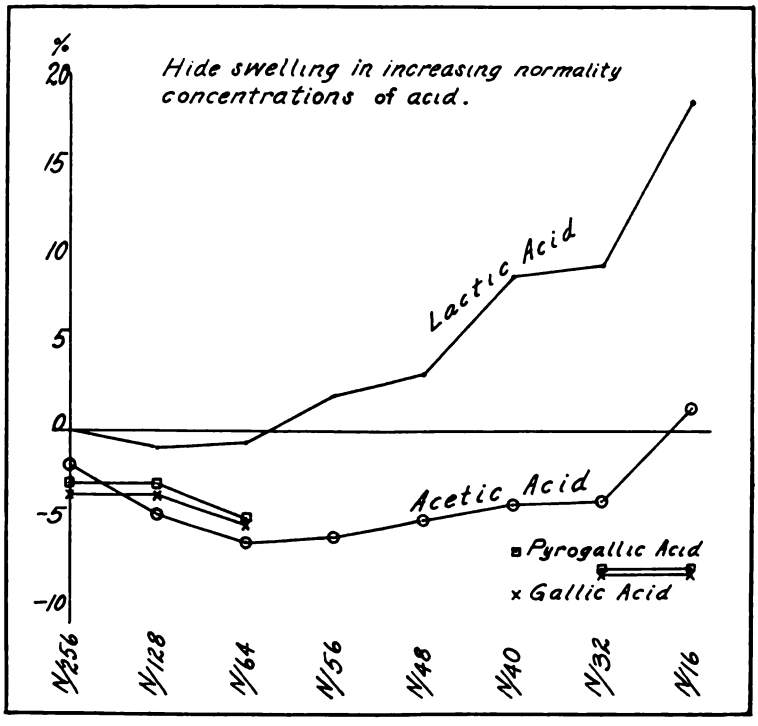

Fig. 2.

Table I is illustrated diagramatically in Fig. 1. These facts, as illustrated in Table I and Fig. 1, prove that — in aqueous solution — lactic acid swells white hide, while the other three acids deplete it, when concentrations are employed which would nor-

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mally occur in tanning practice. This conclusion is further proved by the results shown in Table II and Fig. 2, where we have employed solutions of equal normalities.

TABLE II.

Concentration	Lactic Per cent.	Acetic Per cent.	Gallic Per cent.	Pyrogallic Per cent.
N/256.....	even	—2.0	—3.7	—3.0
N/128.....	—1.0	—5.0	—3.7	—3.0
N/ 64.....	—0.8	—6.3	—5.3	—5.3
N/ 56.....	+2.0	—6.0		
N/ 48.....	+3.3	—5.0		
N/ 40.....	+8.7	—4.3		
N/ 32.....	+9.3	—4.0	—8.0	—7.7
N/ 16.....	+18.5	+1.3	—8.0	—7.7

We will show that the action of these acids in aqueous solution upon white hide is similar to their action thereon when they are present in tannin solutions.

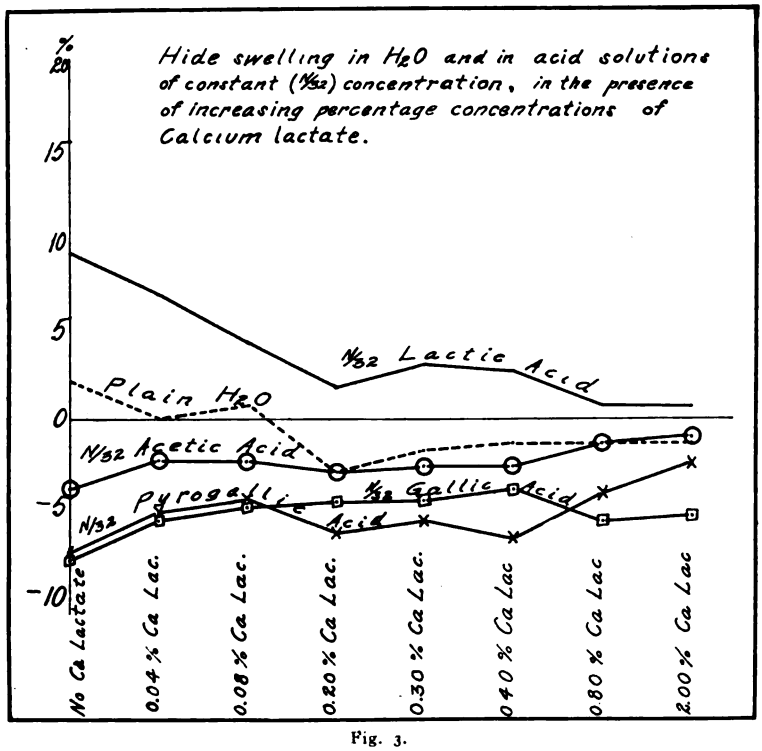

Fig. 3.

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Another item of importance in tan liquor is its mineral content. This is composed mainly of lime, which is particularly true of the early rocker liquors, which have come into contact with the white hide. In such liquors the lime of the hide has been partially dissolved by the organic acids of the liquor, forming calcium lactate and calcium acetate, the proportions of these salts varying with the kind of acid in the liquor. In Table III is shown the effect of various percentage concentrations of calcium lactate, both in plain aqueous solution, and when dissolved in N/32 solution of the four acids, as shown. In other words: we have a constant acid concentration in the presence of increasing lactate concentration. These findings are diagramatically illustrated in Fig. 3. Similar experiments, with calcium acetate, are shown in Table IV and Fig. 4.

TABLE III.

Concentration of calcium lactate	Plain H_2O Per cent.	N/32 Lactic acid Per cent.	N/32 Acetic acid Per cent.	N/32 Gallic acid Per cent.	N/32 Pyrogallic acid Per cent.
None.....	+2.0	+9.3	—4.0	—8.0	—7.7
00.04.....	even	+7.0	—2.3	—5.7	—5.2
00.08.....	+0.7	+4.3	—2.3	—5.0	—4.8
00.20.....	—3.0	+1.7	—3.0	—4.8	—6.5
00.30.....	—1.7	+3.0	—2.7	—4.7	—5.7
00.40.....	—1.3	+2.7	—2.7	—4.0	—6.8
00.80.....	—1.3	+0.7	—1.3	—5.8	—4.2
02.00.....	—1.3	+0.7	—1.0	—4.5	—2.5

TABLE IV.

Concentration of calcium acetate	Plain H_2O Per cent.	N/32 Lactic acid Per cent.	N/32 Acetic acid Per cent.	N/32 Gallic acid Per cent.	N/32 Pyrogallic acid Per cent.
None.....	+2.0	+9.3	—4.0	—8.0	—7.7
00.04.....	+0.7	+5.3	—4.7	—12.0	—7.3
00.08.....	—1.2	+1.2	—3.3	—11.0	—8.7
00.20.....	—2.1	—0.7	—3.3	—11.7	—8.0
00.30.....	—2.5	—3.3	—3.0	—11.7	—8.3
00.40.....	—2.7	—4.0	—3.0	—11.0	—6.7
00.80.....	—3.2	—3.3	—3.0	—11.0	—6.7
02.00.....	—2.8	—1.7	—5.0	—8.0	—6.3

Table III and Fig. 3 show that aqueous solution of calcium lactate depletes white hide; that it has a marked restraining effect upon the swelling power of lactic acid, but does not cause additional depletion in the case of acetic, gallic and pyrogallic acids.

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Table IV and Fig. 4 show that aqueous solution of calcium acetate depletes white hide; is intensely powerful in restraining the swelling power of lactic acid; is comparatively inactive towards acetic and pyrogallic acids, while it greatly increases the depleting power of gallic acid, and to a much greater extent than does lactate.

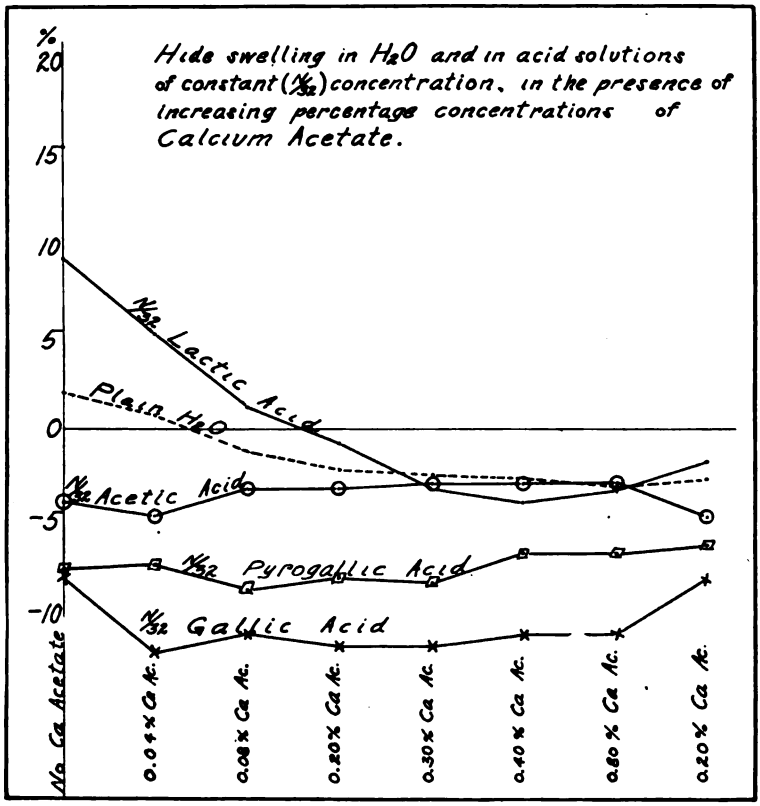

Fig. 4.

We will now take up the effect of each of the four acids upon each other. In Table V and Fig. 5 is shown the action of varying proportions of N/32 lactic and N/32 acetic acids upon white hide.

Table V and Fig. 5 show that acetic acid represses the swelling effect of lactic, and that such repression is progressive with increasing proportions of acetic.

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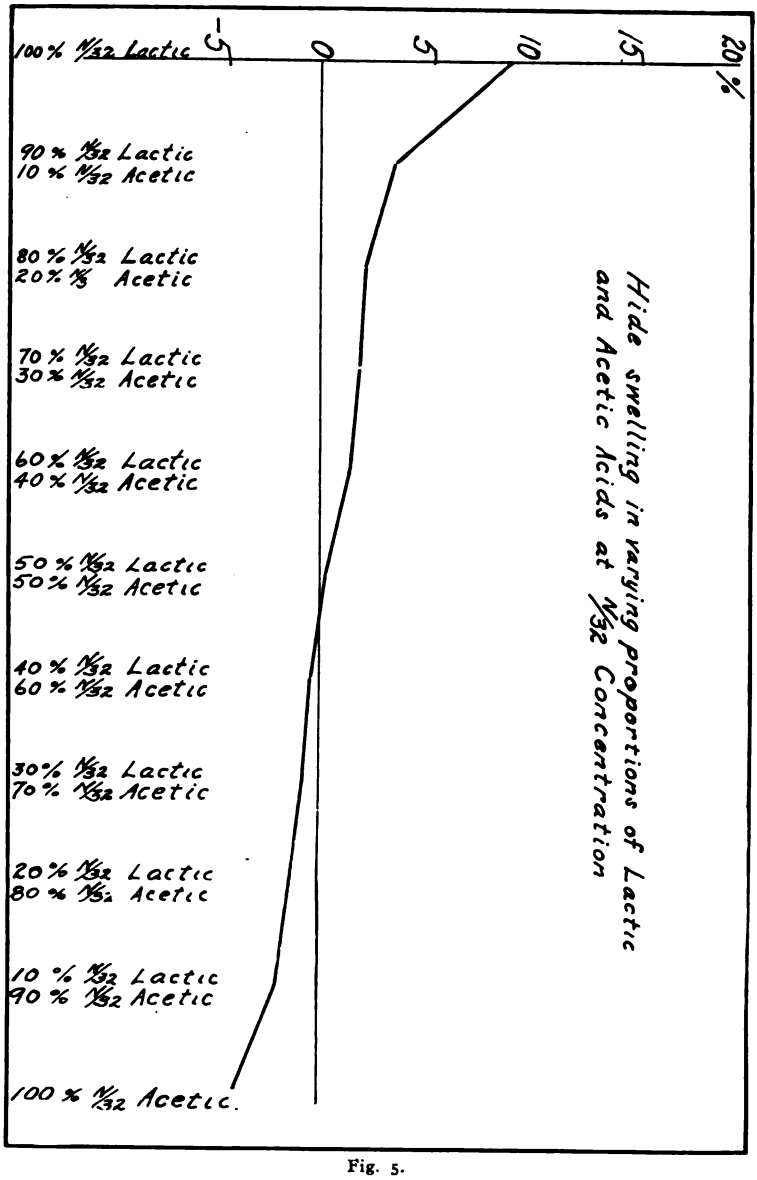

Fig. 5.

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TABLE V.

Per cent.					Per cent.				Per cent.
100	N/32	Lactic	Acid	.....					+9.3
90	"	"	"	plus	10	N/32	Acetic	Acid.	+3.7
80	"	"	"	"	20	"	"	"	+2.3
70	"	"	"	"	30	"	"	"	+2.0
60	"	"	"	"	40	"	"	"	+1.5
50	"	"	"	"	50	"	"	"	+0.3
40	"	"	"	"	60	"	"	"	—0.3
30	"	"	"	"	70	"	"	"	—0.7
20	"	"	"	"	80	"	"	"	—1.3
10	"	"	"	"	90	"	"	"	—2.0
.....					100	"	"	"	—4.0

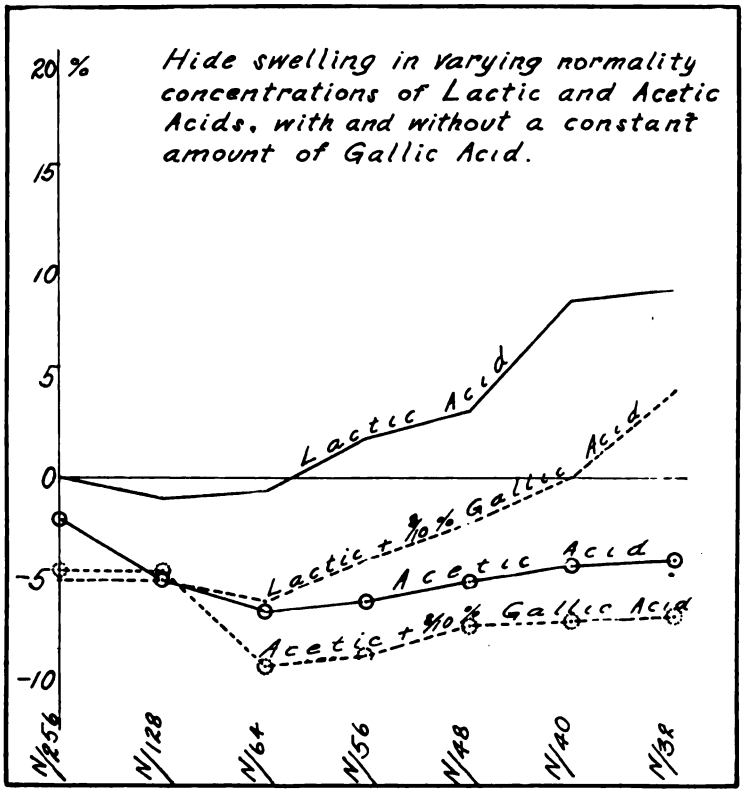

Fig. 6.

In Table VI and Fig. 6 are shown the results of employing a constant concentration of gallic acid (0.8 per cent.), dissolved in increasing normality concentrations of lactic and acetic acid, together with figures showing the action of these acids in the absence of gallic.

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TABLE VI.

Concentration	Plain lactic Per cent.	Lactic plus 0.8 per cent. gallic Per cent.	Plain acetic Per cent.	Acetic plus 0.8 per cent. gallic Per cent.
N/256	even	—5.0	—2.0	—4.5
N/128	—1.0	—5.0	—5.0	—4.7
N/ 64	—0.8	—6.0	—6.3	—9.3
N/ 56	+2.0	—4.0	—6.0	—8.7
N/ 48	+3.3	—2.3	—5.0	—7.3
N/ 40	+8.7	even	—4.3	—7.0
N/ 32	+9.3	+4.3	—4.0	—6.7

Table VI and Fig. 6 show that gallic acid has a powerful depleting action in the presence of lactic acid and that it either increases the depleting action of acetic, or adds its own effect to that of the acetic.

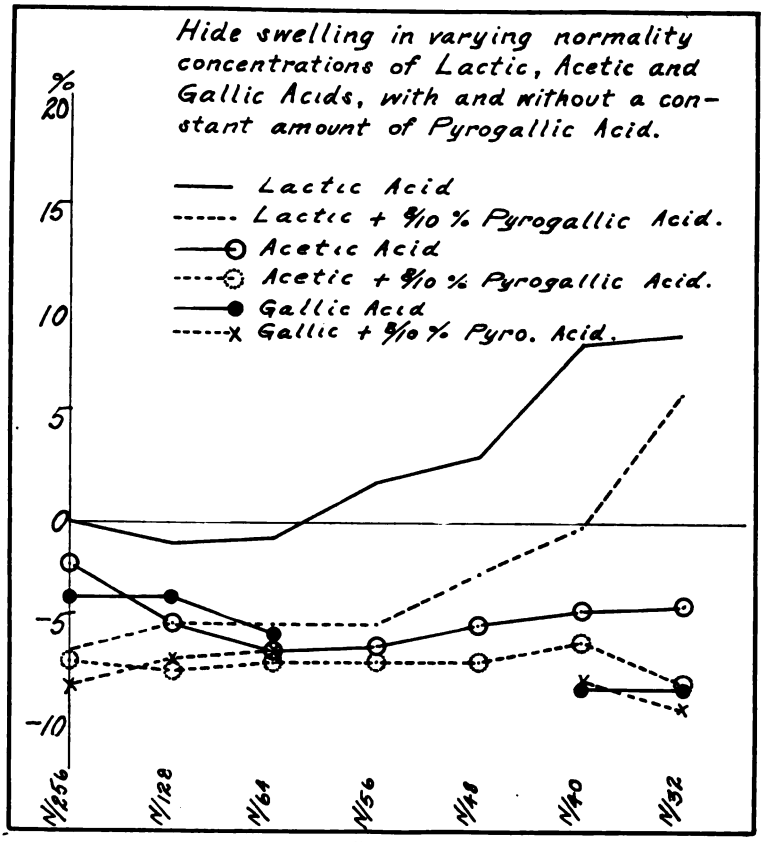

Fig. 7.

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Table VII and Fig. 7 illustrate experiments similar to those in Table VI and Fig. 6, except that pyrogallic acid is substituted for gallic.

TABLE VII.

Concentration	Plain lactic Per cent.	Lactic plus 0.8 per cent. pyrogallic Per cent.	Plain acetic Per cent.	Acetic plus 0.8 per cent. pyrogallic Per cent.	Plain gallic Per cent.	Gallic plus 0.8 per cent. pyrogallic Per cent.
N/256.....	even	—6.3	—2.0	—6.7	—3.7	—8.0
N/128.....	—1.0	—5.0	—5.0	—7.3	—3.7	—6.7
N/ 64.....	—0.8	—5.0	—6.3	—6.7	—5.3	—6.3
N/ 56.....	+2.0	—5.0	—6.0	—6.7		
N/ 48.....	+3.3	—2.5	—5.0	—6.7		
N/ 40.....	+8.7	—0.3	—4.3	—5.7	—8.0	—7.7
N/ 32.....	+9.3	+6.3	—4.0	—7.7	—8.0	—9.0

Table VII shows that pyrogallic acid has a powerful depleting effect in the presence of lactic acid; that it either increases the depleting effect of acetic, or adds its own effect to that of the acetic, and that it does not greatly influence the action of gallic.

We will now study the effect of various ingredients dissolved in tannin solutions. Table VIII gives the result of soaking white hide in different tannin solutions of increasing tannin content. These solutions were all freshly prepared in the laboratory and used immediately. The required amount of lactic acid was added to each to produce an N/16 solution. The quebracho used throughout all of our experiments was the treated, liquid extract.

TABLE VIII.

Per cent.	Myrabs. Per cent.	Queb. Per cent.	Ches. Per cent.	Valonea cups Per cent.	Wattle Per cent.	Ches. oak bark Per cent.	Divi-divi Per cent.
N/ 16 Lactic — no tannin	+18.5	do	do	do	do	do	do
" " plus 0.05 "	+15.5	+15.3	+14.0	+15.2	+18.3	+15.0	+18.0
" " " 0.10 "	+16.5	+13.7	+16.5	+13.0	+17.0	+12.0	+16.0
" " " 0.15 "	+15.7	+13.0	+16.2	+13.2	+18.5	+14.0	+15.0
" " " 0.20 "	+15.0	+14.2	+13.0	+12.8	+12.8	+13.3	+15.0
" " " 0.50 "	+10.0	+10.5	+12.0	+12.3	+13.0	+14.0	+17.0

Table VIII is illustrated diagramatically in Fig. 8.

We do not wish to be misunderstood: the figures shown in Tables VIII and IX represent no attempt to express the ultimate value of the different tanning materials in actual tanning. However, in order to obtain any intelligent idea of the combinations

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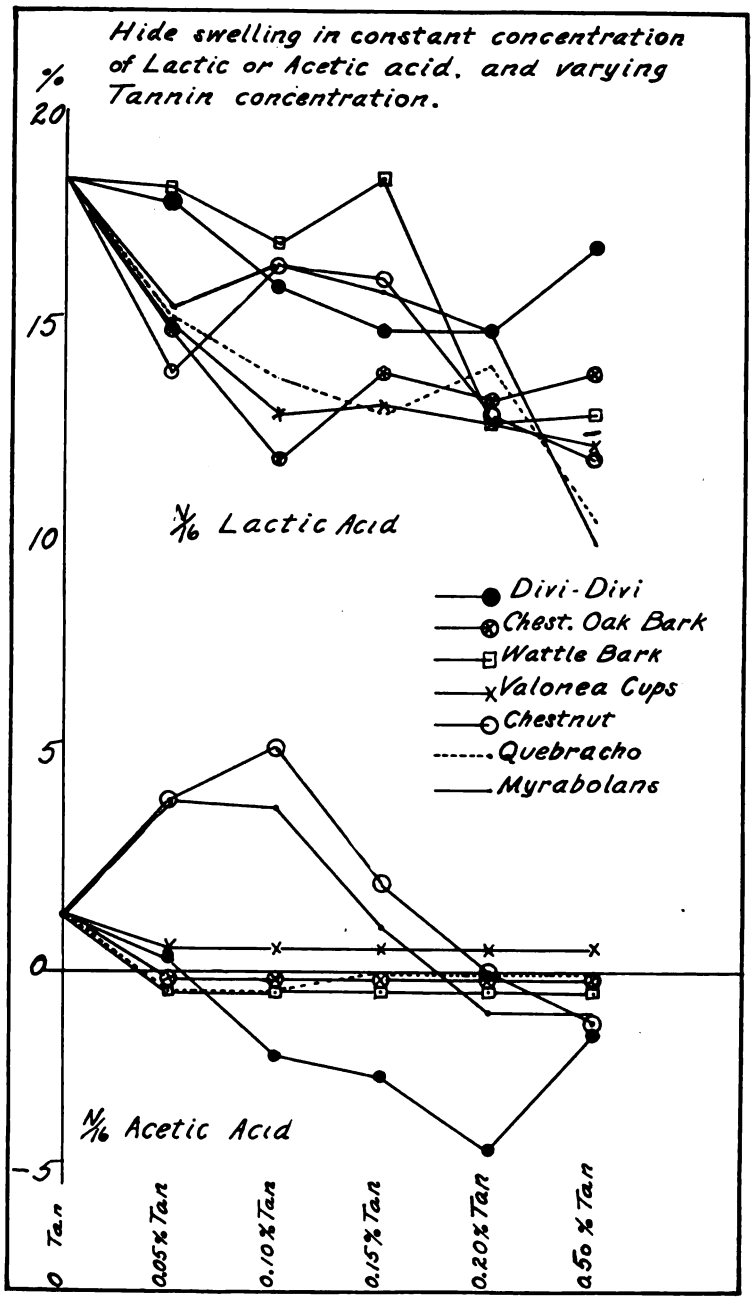

Fig. 8.

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and behavior of the original tan liquor, we must first study it in a pure state. We have thus laid the foundation of an understanding of the same liquor after it has been acted upon by yard conditions or admixture with other tanning materials.

TABLE IX.

		Per cent.		Myrabs. Per cent.	Queb. Per cent.	Ches. Per cent.	Valonea cups Per cent.	Wattle Per cent.	Ches. oak bark Per cent.	Divi-divi Per cent.
N/16	Acetic	— no	tannin	+1.3	do	do	do	do	do	do
"	"	plus 00.05	"	+4.0	—0.5	+4.0	+0.5	—0.5	—0.2	+0.3
"	"	" 00.10	"	+3.7	—0.5	+5.2	+0.5	—0.5	—0.2	—2.0
"	"	" 00.15	"	+1.0	even	+2.0	+0.5	—0.5	—0.2	—2.5
"	"	" 00.20	"	—1.0	even	even	+0.5	—0.5	—0.2	—4.2
"	"	" 00.50	"	—1.0	even	—1.2	+0.5	—0.5	—0.2	—1.5

Table IX is illustrated diagramatically on the lower portion of Fig. 8.

Table VIII shows that in the presence of one-half per cent. tannin of many materials, the swelling power of N/16 lactic acid is partially repressed. Table IX shows that, except for some notable exceptions, the slight swelling effect of N/16 acetic acid is adversely affected by the presence of tannin compounds.

The next question is; whether by increasing the tannin strength of liquor we can entirely eliminate the swelling power of acids. Table X shows the result of soaking white hide in a constant concentration of lactic acid (N/16) in the presence of tannin increments — up to 5.0 per cent.

TABLE X.

Per cent.	Chestnut no acid Per cent.	Chestnut plus acid Per cent.	Quebracho no acid Per cent.	Quebracho plus acid Per cent.
1 Tannin.....	+3.0	+11.0	+3.3	+14.0
2 "	+4.0	+8.3	+3.3	+7.3
3 "	+3.3	+7.6	+3.3	+4.0
4 "	+4.3	+6.7	+3.3	+4.0
5 "	+6.3	+6.3	+4.0	+5.3

Table X shows that in the case of chestnut and quebracho, the swelling effect of even so high a concentration as N/16 lactic acid (which is 0.56 per cent.) is largely lost in a 5 per cent. tannin liquor. We are speaking here solely in respect to swelling and not to other effects of the acid on the liquor, which we will describe later. The figures of Table X are illustrated diagramatically in Fig. 9.

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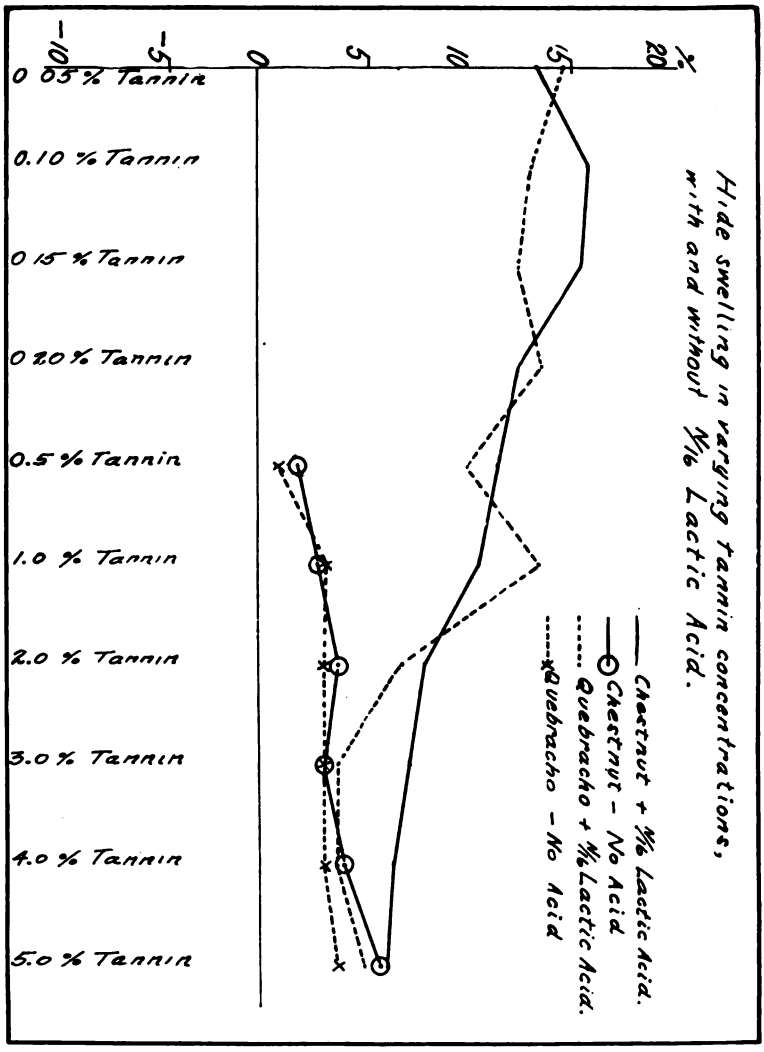

Fig. 9.

TABLE XI.

Per cent.	Chestnut no acid Per cent.	Chestnut plus acid Per cent.	Quebracho no acid Per cent.	Quebracho plus acid Per cent.
1 Tannin.....	+3.0	even	+3.3	+0.7
2 "	+4.0	+2.0	+3.3	+2.0
3 "	+3.3	+2.6	+3.3	+2.0
4 "	+4.3	+4.0	+3.3	+3.3
5 "	+6.3	+4.7	+4.0	+3.3

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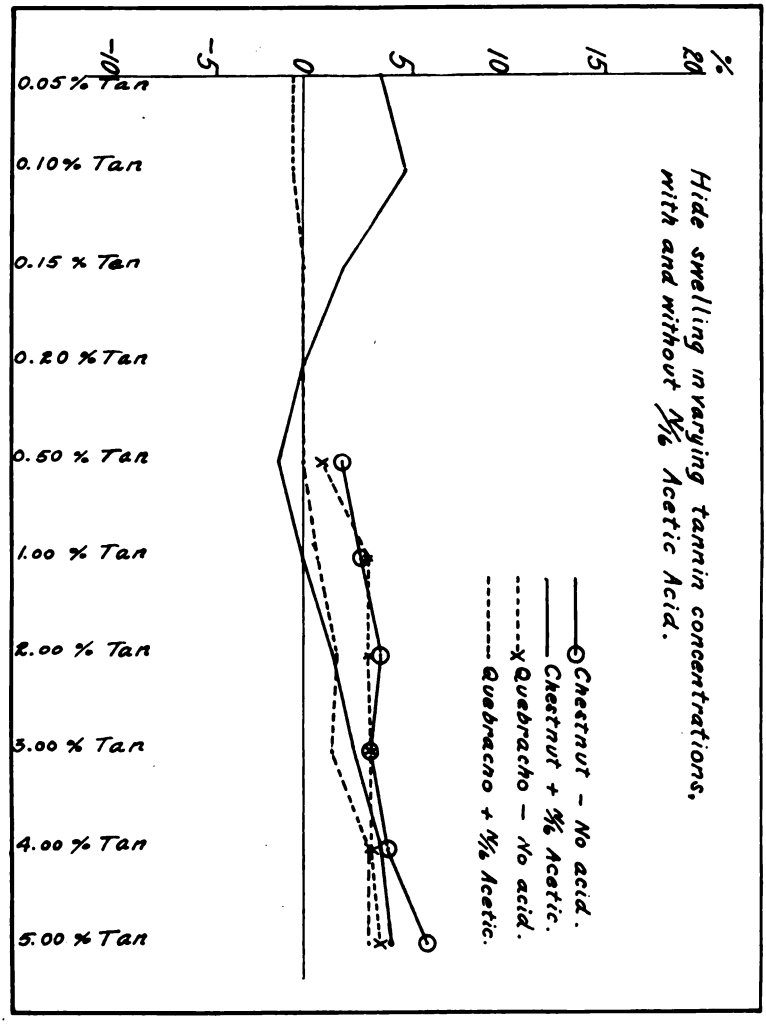

Fig. 10.

Table XI shows the effect of N/16 acetic acid under the same conditions as outlined for Table X.

Table XI shows that N/16 acetic acid (38/100 per cent.) actually depletes in the presence of appreciable amounts of tannin. Table XI is illustrated diagrammatically in Fig. 10.

Having considered the effect of tan liquor, with and without added acid, let us study the action of the *non tan filtrate,* obtained

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by detannization with dry, unchromed hide powder. We have already referred to a tail rocker liquor, in which white hide lost 3 per cent. in weight. Adding lactic acid to the non tan filtrate of this liquor, so that the system has increasing concentration of added acid, we secure a very interesting action on white hide. These results are shown in Table XII, which include, also, similar experiments with the non tan filtrate of a head rocker, fresh leach liquor and other fresh materials, all of which were diluted to 0.5 per cent. tannin and then detannized.

TABLE XII.

	Plain H_2O	Tail rocker	Head rocker	Fresh leach liq.	Ches. oak bark	Ches.	Queb.
Straight non tan liq. — No Acid	.....	—3.0	—4.7	—2.3	—4.3	—3.3	—0.6
" plus acid to N/256	even	—2.0	—3.0	—3.7	—3.3	—2.7	—1.3
" " " " N/128		—1.0	—1.3	—3.0	—3.3	—2.3	—4.7	—2.0
" " " " N/ 64		—0.8	—1.3	—4.3	—4.0	—2.3	—3.0	—2.0
" " " " N/ 32		+9.3	—1.0	—0.6	+2.8	—1.0	+2.3	—0.6
" " " " N/ 16		+18.5	+3.0	+7.4	+10.7	+9.3	+12.3	+10.7

Soaking white hide in the original tail rocker already referred to, caused it to lose 3 per cent. in weight; soaking it in the non tan filtrate shows 3 per cent. weight loss. The straight head rocker, diluted to ½ per cent. tannin caused a gain of 2.7 per cent; its non tans a loss of 4.7 per cent; fresh leach liquor a gain of 2.0 per cent., and its non tans a loss of 2.3 per cent; chestnut oak bark a gain of 0.3 per cent., and its non tans a loss of 4.3 per cent; chestnut a gain of 1.0 per cent. and non tans a loss of 3.3 per cent; while quebracho shows a gain of 1.0 per cent., and its non tans a loss of 0.6 per cent. We will return later to the significance of these various findings.

We may next inquire as to the "mellowness" or "astringency" of a vegetable tan liquor. By the former term we mean a liquor which tans slowly and evenly and produces a relatively attractive color and a smooth feeling grain. By the latter term we mean the opposite of these qualities. If we place white hide in a fresh chestnut oak bark, chestnut or quebracho liquor, we obtain a dark, rough, unsightly, case-hardened leather. If the same liquor has passed down through the yard, however, by the time it reaches the early rockers it has become mellowed. This is usually attributed to the gradual increase of its non tan content and proportionate

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decrease in "purity." This explanation is correct—as far as it goes. In Tables XIII, XIV and XV we have employed ½ per cent. tannin solutions throughout, in which we have dissolved the various acids and salts as indicated; we have then soaked white hide in each solution, under the same condtions covering previous experiments.

Deductions.

Having gathered certain facts let us consider their significance.

The first feature commanding attention is the thought that a vegetable tan liquor cannot be regarded as an entity, but that it may possess various chemical and physical properties, whose combination and inter-action determine its relation to the finished product: leather.

If we consider them singly and start with lactic acid, we note that: (1) this acid has great swelling power, (2) it has a mellowing effect upon astringent liquors, (3) when in combination with chestnut and quebracho fresh liquor, it does not darken color or precipitate liquor until a rather high concentration has been exceeded; and in the case of chestnut oak bark, even 2 per cent. of lactic acid causes no precipitation, (4) when it comes into contact with limed hide the calcium lactate formed has less depleting action upon the hide, either in itself or in its repression of the swelling of lactic acid, than has calcium acetate, and (5) viewed from a physiological standpoint, lactic acid is a "natural" acid for protein, as evidenced by the fact that protracted muscular activity in a normal animal body is followed by the formation of large quantities of lactic acid, without subsequent injury to such an organism.

Acetic acid has: (1) little or no swelling power, (2) it has great mellowing power on certain astringent tan liquors, (3) it represses the swelling power of lactic acid tremendously, (4) it aggravates the depleting power of gallic acid and, (5) it delimes white hide, forming calcium acetate, which has tremendous depleting power, both in itself and in its repression of lactic swelling and aggravation of the depletion of gallic. NOTE: in a previous publication * we have shown the wide differences in the hydration properties of the combination of various acids and alkalies with white hide; and there stated our conception of the

* This JOURNAL, Vol. XV, No. 4.

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TABLE XIII.—Chestnut.

Lactic Acid.

Straight		0.5 %	tan sol.	+1.0%	poor color, rough grain
"	plus	00.04%	acid	—0.3%	distinct color improv.
"	"	00.08%	"	—0.3%	greater color improv.
"	"	00.20%	"	—2.3%	still greater color improv.
"	"	00.30%	"	+1.0%	still greater color improv.—some precip.
"	"	00.40%	"	+7.3%	poor color—much precip.
"	"	00.80%	"	+14.7%	very poor color—much precip.
"	"	02.00%	"	+25.7%	very poor color—heavy precip.

Gallic Acid.

Straight		0.5 %	tan sol.	+1.0%	poor color, rough grain
"	plus	00.04%	acid	—0.3%	poor color, rough grain
"	"	00.08%	"	—0.3%	poor color, rough grain
"	"	00.20%	"	—0.3%	remarkable color improv.
"	"	00.30%	"	—2.0%	greater color improv.
"	"	00.40%	"	—2.0%	still greater color improv.
"	"	00.80%	"	—3.0%	fine color
"	"	02.00%	"	—3.0%	fine color

Note: there was no precipitation of the liquor by the different concentrations of gallic.

Acetic Acid.

Straight		0.5 %	tan sol.	+1.0%	poor color, rough grain
"	plus	00.04%	acid	—2.0%	slight color improv.
"	"	00.08%	"	—1.7%	more color improv.
"	"	00.20%	"	—2.3%	fairly good color
"	"	00.30%	"	—2.0%	good color
"	"	00.40%	"	—2.3%	good color
"	"	00.80%	"	+7.3%	good color
"	"	02.00%	"	+15.3%	poor color

Note: there was no particular precipitation of the liquor by the different concentrations of acetic.

Pyrogallic Acid.

Straight		0.5 %	tan sol.	+1.0%	poor color, rough grain
"	plus	00.04%	acid	—0.3%	no color change
"	"	00.08%	"	—2.0%	no color change
"	"	00.20%	"	—2.0%	no color change
"	"	00.30%	"	—2.7%	no color change
"	"	00.40%	"	—2.7%	no color change
"	"	00.80%	"	—3.3%	no color change
"	"	02.00%	"	—3.3%	no color change

Note: there was no precipitation of the liquor by the different concentrations of pyrogallic.

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TABLE XIII.—CHESTNUT—(*Continued*)

CALCIUM LACTATE.

Straight		0.5 %	tan sol.	+1.0%	poor color, rough grain
"	plus	00.04%	lact.	—0.5%	no color change
"	"	00.08%	"	—1.5%	no color change
"	"	00.20%	"	—1.2%	color much improved
"	"	00.30%	"	—2.7%	color further improv., considerable precip.
"	"	00.40%	"	—1.8%	color more improved, much precip.
"	"	00.80%	"	—2.8%	color further improv., heavy precip.
"	"	02.00%	"	—1.2%	color further improv., very heavy precip.

CALCIUM ACETATE.

Straight		0.5 %	tan sol.	+1.0%	poor color, rough grain
"	plus	00.04%	acetate	—3.3%	no color change
"	"	00.08%	"	—4.0%	no color change
"	"	00.20%	"	—1.0%	color improved, some precip.
"	"	00.30%	"	—3.3%	color further improv., more precip.
"	"	00.40%	"	—4.3%	color light but not uniform, owing to heavy precip.
"	"	00.80%	"	—3.7%	same as 00.04%.
"	"	02.00%	"	—4.7%	same as 00.04%.

TABLE XIV.—QUEBRACHO.

LACTIC ACID.

Straight		0.5 %	tan sol.	+1.5%	poor color, rough grain
"	plus	00.04%	acid	—0.3%	no color change
"	"	00.08%	"	+1.0%	slight color change
"	"	00.20%	"	+0.7%	good color
"	"	00.30%	"	+0.3%	fine color
"	"	00.40%	"	+3.0%	fine color, some precip.
"	"	00.80%	"	+15.3%	fine color, some precip.
"	"	02.00%	"	+17.3%	fine color, some precip.

ACETIC ACID.

Straight		0.5 %	tan sol.	+1.5%	poor color, rough grain
"	plus	00.04%	acid	+0.8%	color improved
"	"	00.08%	"	+0.7%	color more improved
"	"	00.20%	"	+1.3%	color still more improv.
"	"	00.30%	"	even	greater color improv.
"	"	00.40%	"	+3.0%	still more color improv.
"	"	00.80%	"	+5.0%	further color improv.

Note: there was no precipitation of the liquor by the different concentrations of acetic.

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TABLE XIV.—QUEBRACHO—(*Continued*)

GALLIC ACID.

Straight		0.5 %	tan sol.	+1.5%	poor color, rough grain
"	plus	00.04%	acid	+1.0%	no color change
"	"	00.08%	"	—1.0%	no color change
"	"	00.20%	"	—1.0%	marked color improv.
"	"	00.30%	"	—1.0%	further color improv.
"	"	00.40%	"	—2.0%	more color improv.
"	"	00.80%	"	—3.0%	still more color improv.
"	"	02.00%	"	—2.0%	still more color improv.

Note: there was no precipitation of the liquor by the different concentrations of gallic.

CALCIUM LACTATE.

Straight		0.5 %	tan sol.	+1.5%	poor color, rough grain
"	plus	00.04%	lact.	+1.2%	no color change
"	"	00.08%	"	+0.5%	no color change, much precip.
"	"	00.20%	"	—2.0%	no color change, much precip.
"	"	00.30%	"	—2.1%	marked color improv., much precip.
"	"	00.40%	"	—1.8%	more color improv., much precip.
"	"	00.80%	"	—2.5%	further color improv., much precip.
"	"	02.00%	"	—1.7%	more color improv., much precip.

PYROGALLIC ACID.

Straight		0.5 %	tan sol.	+1.5%	poor color, rough grain
"	plus	00.04%	acid	even	no color change
"	"	00.08%	"	—1.0%	no color change
"	"	00.20%	"	—2.7%	no color change
"	"	00.30%	"	—2.3%	no color change
"	"	00.40%	"	—2.3%	color improved
"	"	00.80%	"	—3.0%	color improv. further
"	"	02.00%	"	—2.3%	color improv. still more

Note: as shown above, starting with 00.40%, there is color improvement. This, however, is temporary; the specimens darken rapidly upon exposure to air.

CALCIUM ACETATE.

Straight		0.5 %	tan sol.	+1.5%	poor color, rough grain
"	plus	00.04%	acetate	—0.3%	no color change
"	"	00.08%	"	—3.3%	no color change, much precip.
"	"	00.20%	"	—2.7%	no color change, much precip.
"	"	00.30%	"	—4.3%	improved color, much precip.
"	"	00.40%	"	—5.0%	improved color, much precip.
"	"	00.80%	"	—5.0%	improved color, much precip.
"	"	02.00%	"	—4.7%	improved color, much precip.

Note: the color improvement noted above disappears upon exposure to air, becoming dark and unsightly.

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TABLE XV.—Chestnut Oak Bark.

Lactic Acid.

Straight		0.5 %	tan sol.	+0.5%	poor color, rough grain
"	plus	00.04%	acid	+0.5%	no color change
"	"	00.08%	"	+0.3%	color much improved
"	"	00.20%	"	+1.7%	color more improved
"	"	00.30%	"	+4.7%	color still more improv.
"	"	00.40%	"	+11.1%	color further improved
"	"	00.80%	"	+19.2%	poor, dark color
"	"	02.00%	"	+18.0%	poor, dark color

Note: no precipitation is caused by the various concentrations of lactic acid.

Gallic Acid.

Straight		0.5 %	tan sol.	+0.5%	poor color, rough grain
"	plus	00.04%	acid	even	no color change
"	"	00.08%	"	even	no color change
"	"	00.20%	"	—0.7%	color improved
"	"	00.30%	"	—3.7%	color much improved
"	"	00.40%	"	—4.0%	color further improved
"	"	00.80%	"	—4.0%	color still further improved
"	"	02.00%	"	—3.3%	color improv. greater

Note: no precipitation is caused by the various concentrations of gallic acid.

Acetic Acid.

Straight		0.5 %	tan sol.	+0.5%	poor color, rough grain
"	plus	00.04%	acid	—1.7%	improved color
"	"	00.08%	"	—3.0%	color much improved
"	"	00.20%	"	—3.3%	color more improved
"	"	00.30%	"	—1.0%	color still further improved
"	"	00.40%	"	—0.3%	color still more improv.
"	"	00.80%	"	+4.0%	color still further improved
"	"	02.00%	"	+8.7%	color still further improved

Note: no precipitation is caused by the various concentrations of acetic acid.

Pyrogallic Acid.

Straight		0.5 %	tan sol.	+0.5%	poor color, rough grain
"	plus	00.04%	acid	—1.3%	color dark and poor
"	"	00.08%	"	—0.7%	color dark and poor
"	"	00.20%	"	—2.7%	color dark and poor
"	"	00.30%	"	—3.3%	color dark and poor
"	"	00.40%	"	—2.7%	color dark and poor
"	"	00.80%	"	—4.0%	color dark and poor
"	"	02.00%	"	—3.3%	color dark and poor

Note: no precipitation is caused by the various concentrations of pyrogallic acid. While there is no color improvement throughout, yet, starting with 00.20%, there is a noticeable slowing up of penetration and the grain is smoother.

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laws governing such phenomena. In this article additional proof is brought, *viz.*, that calcium protein lactate is a very different compound from calcium protein acetate.

Gallic acid has: (1) great depleting power; both in itself, and in its repression of the swelling of lactic, and its aggravation of the depletion of acetic; and (2) it has considerable mellowing properties with some astringent liquors.

Pyrogallic acid has properties quite similar to gallic, except that its lightening of the color given to leather by formerly astringent liquors is a temporary change. However, it is not known how widely this acid is distributed, and when it does occur in tan liquors, whether its concentration is great.

Calcium lactate has: (1) a marked depleting action on white hide, both in itself and in its repression of lactic swelling, and is comparatively inactive towards acetic; (2) it mellows certain astringent liquors; and, (3) it precipitates certain tanning materials, when added to them in concentration beyond a certain optimum.

Calcium acetate has: (1) a greater depleting action on white hide than has the lactate, both in itself and in its repression of the swelling of lactic acid; is comparatively inert towards the action of acetic, and aggravates the action of gallic; and, (2) it mellows chestnut and quebracho and has a precipitating action when so doing.

In the foregoing paragraphs, where we have used the term "mellowing," it is synonomous with the point of a definite lightening of the color of the partly tanned hide, compared with that tanned in the original tan liquor. Such a color change is invariably accompanied by the other characteristics of a mellow liquor — in as far as these experiments are concerned. In comparing our results with actual tannery conditions, the fact that our experiments cover a twenty-four hour period and that layaways cover days or weeks must be kept in mind.

Practical Applications.

The experiments and deductions herein outlined have some interesting practical corollaries.

Every modern tanner knows that lactic acid is a safe and desirable material; both for deliming white hide, and for adding to tan

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liquors, in moderate quantity. We trust we have shown some of the reasons for this, besides demonstrating how strong a fresh liquor may be and still allow added acid to swell hide. Addition of lactic acid to the stronger liquors reflects itself in the changed character of such a liquor; as well as in its swelling and deliming power, as it passes through the rockers. The amount of lactic acid, and the point at which it should be added, is a matter to be worked out in each tannery, according to local conditions.

Many tanners know the danger of excess of acetic acid. Some learned through adding the acid direct to their liquors; other by using an excess of myrobalans—when their yard went "too sour;" while others learned through the use of chestnut which had been insufficiently concentrated. Each of these educational methods was expensive. By "insufficiently concentrated" we mean that when chestnut (which is certainly a highly valuable tanning material) is not carried to the usual 25 per cent. tannin concentration or powdered form, it produces excess of acetic acid in the yard; and flat, tinny leather results.

Some tanners have found that when an abnormally high ash content in their liquors has been reduced, their leather becomes plumper and more solid. In other words, they simply removed some of the calcium lactate and acetate and gave the acids of their liquors an opportunity to function.

We know of two instances where excessive gallic acid was present in the rockers; this was evidenced at this point by the rapid color change of the interior of a piece of hide, cut from the early rockers, to the purplish-blue which is characteristic of gallic acid and lime, when exposed to air. The excess of gallic was confirmed, also, by analytical methods. The finished sole leather from such liquors was thin and poorly tanned.

The matter of astringency has been the subject of protracted discussion during recent months. The fact that astringent quebracho may be mellowed through the addition of such a material as gambier, was made use of some years ago by an itinerant "tanning expert." Dr. L. E. Levi* has recently called attention to the fact that as far back as 1897 quebracho was mellowed with nut galls; and Wilson and Kern** have recently shown that

* This JOURNAL, Vol. XV, No. 8.

** This JOURNAL, Vol. XV, No. 5.

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by increasing the non tan content of quebracho with gallic acid, a mellowness similar to that of gambier results. Every tanner knows that as a fresh liquor passes down the yard it becomes lower in purity and more mellow. A few tanners have taken advantage of the addition of lactic acid to the new and highly astringent liquors of a newly built tannery and so mellowed them quite satisfactorily.

Referring to Tables XIII, XIV and XV, where we have employed solutions of ½ per cent. tannin throughout, the various materials are mellowed as follows:

Chestnut by	Quebracho by	Ches. oak bark by
00.04 lactic acid	00.20	00.08
00.20 acetic "	00.08	00.08
00.20 gallic "	00.20	00.20
00.20 calcium lactate	00.30	
00.20 " acetate.....	00.30	

Proposed Method.

Our present knowledge — and lack of knowledge — of vegetable tanning conditions ordains that a successful tanner is he, who, given a good beam house condition, maintains a ceaseless striking of the proper balance between astringency and mellowness of liquor and neither overfeeds nor underfeeds his stock. In modern tannage he must maintain the proper equilibrium of tannin unit components. It is evident that if the chemist is to render him more active service, he must be able to state — with some degree of definiteness—whether a given liquor will swell or deplete white hide and whether it is mellow or astringent. The method we have outlined in the preceeding pages makes this possible, without interfering with any other methods, such as acid determination, which experience has shown to be valuable for routine control.

The use of white hide does away with all assumptions and corrections, for we thus deal with the same hide and hide condition as in the tannery. We may take samples of each liquor in the yard and by soaking white hide in them, and in their non tans, we obtain certain arbitrary results. These results can be compared with a portion of the same hide soaked in lactic acid, of a chosen concentration. Different hides may vary in their hydration etc., but we obviate this objection by always having a comparison with the lactic acid swelling. If we have such figures

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on yard liquors during a period when observation and accounting records show the yard gain and leather quality to have been good, we can detect subsequent changes in the yard.

At the beginning of this article we asked why the tail rocker we described caused hide to lose 3 per cent. in weight. Knowing that it contains acetic, gallic, pyrogallic, a small amount of lactic acid, along with about one per cent. of calcium acetate, we are now in a position to understand its depletion of white hide.

LABORATORY
OF
ASHLAND LEATHER COMPANY,
ASHLAND, KENTUCKY.

THE DETERMINATION OF WATER SOLUBLE IN LEATHER 1920 COMMITTEE REPORT.*

By G. L. Terrasse, Chairman, and J. F. Anthes.

The determination of the water soluble content of leather has long been a source of controversy among leather chemists, a fact arising from variations in the methods of analysis used by different operators and by no means due entirely to the "personal equation." It was with the idea of considering the factors which influence the water solubles so as to determine the best conditions for ascertaining a certain figure called "Water Soluble," that this Committee work on this time honored question was continued.

The Committee consisted of the following members:

G. L. Terrassee, Chairman, and J. F. Anthes, American Leather Research Laboratory, 80 South St., New York, N. Y.
S. K. Johnson and F. P. Veitch, Leather and Paper Laboratory, Bureau of Chemistry, Washington, D. C.
F. F. Marshall, Kistler Leather Co., Lock Haven, Pa.
R. E. Porter, Ashland Leather Co., Ashland, Ky.
Paul Hayes, Graton & Knight Laboratories, Worcester, Mass.
L. E. Stacy, C. C. Smoot & Sons Co., N. Wilkesboro, N. C.

Messrs. Marshall and Hayes, the latter due to illness, were unable to contribute to the report.

The following directions were sent to each member of the Committee, by the Chairman:

* Read at the Seventeenth Annual Meeting at Atlantic City, May 28, 1920.

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"It is suggested upon receipt of the sample of ground leather, the moisture and the petroleum ether extractive be determined. That the major part of the sample be petroleum ether extracted; air dried; and the moisture on this air dried extracted portion be determined and this extracted part be sealed in a bottle. In all determinations of water solubles it is suggested that only this ligroin extracted leather powder portion be used and that the apparatus used for water solubles be of the type described by Réed and Churchill in the April, 1919, number of the JOURNAL of the A. L. C. A.; and should you not have accessible a description of this apparatus, the writer will be pleased to furnish details.

"To simplify and reduce work as much as possible the following procedure is suggested.

"I. To digest over night at laboratory temperature (25° C.) and then percolate at 50° and save each successive 100 cc. portion of the percolate, evaporate and weigh separately, and calculate separately to dry ligroin extracted leather powder. This gives us a good line on the influence of continued increasing amounts of water. Use 30 grams of leather powder for each extraction.

"II. Digest for three hours, at laboratory temperature (25° C.) and then proceed exactly as under I. This reduces the total time to six hours instead of approximately fifteen hours as under I.

"III. Proceed as under I with no digestion period at all. This reduces the total time to three hours.

"IV. Digestion over night at laboratory temperature (25° C.) and percolate at 35° C., otherwise as under I. This to study a rather low temperature influence.

"V. Digestion over night at laboratory temperature (25° C.) and percolate at 70° C., otherwise as under I. This to study a rather high temperature influence.

Qualitative iron spot tests may be made for tannin in the various 100 cc. portions and the presence or absence of tannin noted."

The leather sent out from this laboratory to the various members for the determination of Water Soluble, was a finely ground composite sample of four kinds of vegetable tanned sole and belting leather. The percentages of Moisture and Grease in the sample as received by the various members of the Committee are given in Table I.

TABLE I.—PERCENTAGES OF MOISTURE AND GREASE.

Determination	J. F. Anthes	R. E. Porter	S. K. Johnson	L. E. Stacy	Average
Moisture (as rec'd.)	10.18%	10.04%	10.20%	10.40%	10.21%
Grease	2.83%	3.35%	3.33%	3.01%	3.13%

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Some of the factors which come into consideration in determining the Water Soluble content of leather are:

1. The apparatus used in the determination.
2. The condition of the sample used for the water soluble determination.
3. The time of digestion.
4. The temperature of extraction.
5. The time of extraction.
6. The amount of leather extracted.
7. The volume of percolate collected.

The first factor can be made uniform by using the best and hence what should be an official type of apparatus. All aqueous extractions carried on in this laboratory were made in the Churchill-Reed apparatus. This extractor, which is simple in construction, has locally given satisfactory results and at present is being used in many leather laboratories. It is suggested that this extractor be made official.

It is reasonable to surmise and it has been proved true that the presence of grease in leather retards its leaching. Hence it is imperative that the sample of leather which is to be used for the determination of Water Soluble shall be free from grease and finely ground. It is suggested that these two conditions be made official and not left optional with each analyst.

The third factor to be considered is the time of digestion. In the above mentioned instructions sent to the Committee members the times of digestion suggested were three hours, over night and no digestion period. The determinations showing the influence of the time variable are given in Table II, the other conditions prevailing being uniform.

If the results of the four analysts for each time period be averaged it is seen at a glance that the average total extractive is practically the same whether there is no digestion, a three hour period, or an over night digestion.

The fourth factor for consideration is the temperature influence and with a common over night digestion and other conditions uniform, the three temperatures used in percolation were 35° C., 50° C., and 70 C. Table III gives the results at these temperatures.

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TABLE II.—PERCENTAGE OF WATER SOLUBLE ON DRY BASIS.

No. of each successive 100 cc. portion	Digestion over night Extraction at 40° C.				Digestion on three hours Extraction at 50° C.				No digestion Extraction at 50° C.			
	Anthes	Porter	Johnson	Stacy	Anthes	Porter	Johnson	Stacy	Anthes	Porter	Johnson	Stacy
1	11.61%	18.67%	....	16.45%	14.09%	18.80%	....	16.20%	16.22%	18.45%	....	13.71%
2	8.33	3.20	....	3.47	5.50	2.74	....	3.57	3.75	3.30	....	5.22
3	2.85	1.67	....	1.91	2.48	1.61	....	1.96	3.02	1.63	....	2.26
4	1.50	1.17	....	1.31	2.07	1.16	....	1.33	1.46	1.13	....	1.50
5	1.23	0.93	....	1.01	1.19	0.92	....	1.02	1.08	0.88	....	1.12
6	0.91	0.79	....	0.82	0.88	0.78	....	0.82	0.89	0.74	....	0.90
7	0.74	0.70	....	0.70	0.72	0.68	....	0.70	0.70	0.66	....	0.76
8	0.63	0.62	....	0.60	0.64	0.60	....	0.60	0.61	0.58	....	0.65
9	0.54	0.55	....	0.53	0.57	0.53	....	0.53	0.55	0.52	....	0.57
10	0.44	0.48	27.82%	0.47	0.50	0.49	27.26%	0.48	0.50	0.45	27.98%	0.51
11	0.42	0.44	0.48	0.43	0.45	0.44	0.43	0.44	0.43	0.41	0.46	0.46
12	0.41	0.41	0.44	0.38	0.43	0.38	0.44	0.40	0.40	0.38	0.43	0.42
13	0.36	0.37	0.43	0.36	0.39	0.36	0.41	0.37	0.40	0.35	0.40	0.38
14	0.33	0.34	0.40	0.33	0.38	0.33	0.40	0.34	0.35	0.33	0.37	0.36
15	0.31	0.31	0.35	0.30	0.33	0.31	0.37	0.32	0.31	0.31	0.33	0.33
16	0.28	0.30	0.32	0.28	0.29	0.30	0.25	0.30	0.30	0.29	0.31	0.31
17	0.27	0.28	0.32	0.27	0.26	0.28	0.32	0.28	0.26	0.27	0.29	0.29
18	0.23	0.26	0.30	0.26	0.25	0.26	0.32	0.26	0.25	0.25	0.28	0.27
19	0.23	0.25	0.27	0.25	0.25	0.25	0.29	0.24	0.25	0.24	0.26	0.26
20	0.22	0.23	0.25	0.24	0.22	0.23	0.26	0.23	0.24	0.23	0.25	0.24
Total	31.84%	31.97%	31.38%	30.37%	31.89%	31.45%	30.75%	30.39%	31.97%	31.40%	31.36%	30.53%
Average		31.39%				31.16%				31.32%		

In the three Johnson columns under the 10th portion is given the total of the first ten portions.

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TABLE III.—PERCENTAGE OF WATER SOLUBLE ON DRY BASIS.

No. of each successive 100 cc. portion	Digestion over night Extraction at 35° C.			Digestion over night Extraction at 50° C.				Digestion over night Extraction at 70° C.			
	Anthes	Porter	Stacy	Anthes	Porter	Johnson	Stacey	Anthes	Porter	Johnson	Stacy
1	12.15%	16.47%	10.13%	11.61%	18.67%	....	16.45%	12.34%	18.76%	....	17.13%
2	4.49	2.61	3.93	8.33	3.20	....	3.47	8.02	4.31	....	5.36
3	2.21	1.28	2.44	2.85	1.67	....	1.91	2.82	2.42	....	2.39
4	1.61	0.88	1.66	1.50	1.17	....	1.31	2.18	1.59	....	1.52
5	1.09	0.72	1.21	1.23	0.93	....	1.01	2.79	1.14	....	1.13
6	0.85	0.59	0.92	0.91	0.79	....	0.82	1.24	0.86	....	0.87
7	1.09	0.51	0.73	0.74	0.70	....	0.70	2.83	0.69	....	0.73
8	0.67	0.45	0.61	0.63	0.62	....	0.60	0.78	0.58	....	0.61
9	0.54	0.43	0.52	0.54	0.55	....	0.53	0.62	0.50	....	0.52
10	0.48	0.39	0.46	0.44	0.48	27.82%	0.47	0.44	0.43	31.16%	0.46
11	0.43	0.37	0.43	0.42	0.44	0.48	0.43	0.41	0.38	0.39	0.40
12	0.40	0.34	0.39	0.41	0.41	0.44	0.38	0.36	0.34	0.38	0.36
13	0.36	0.32	0.36	0.36	0.37	0.43	0.36	0.33	0.31	0.35	0.35
14	0.33	0.30	0.34	0.33	0.34	0.40	0.33	0.29	0.27	0.32	0.31
15	0.30	0.29	0.32	0.31	0.31	0.35	0.30	0.28	0.24	0.29	0.28
16	0.30	0.28	0.30	0.28	0.30	0.32	0.28	0.25	0.23	0.26	0.26
17	0.26	0.27	0.29	0.27	0.28	0.32	0.27	0.24	0.21	0.25	0.25
18	0.26	0.25	0.27	0.23	0.26	0.30	0.26	0.23	0.18	0.24	0.21
19	0.26	0.24	0.26	0.23	0.25	0.27	0.25	0.21	0.17	0.23	0.20
20	0.24	0.23	0.25	0.22	0.23	0.25	0.24	0.19	0.16	0.21	0.20
Total	28.32%	27.22%	25.82%	31.84%	31.97%	31.38%	30.37%	36.85%	33.77%	34.08%	33.54%
Average		27.12%			31.39%				34.56%		

In the two Johnson columns under the 10th portion is given the total of the first ten portions.

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A study of Table III indicates the pronounced influence of the temperature of extraction, other conditions being equal. The average figures of the amount of water soluble extracted at 35° C. is 27.12 per cent., at 50° C. is 31.39 per cent., and at 70° C. is 34.56 per cent. Unquestionably an arbitrary fixation of the temperature extraction is imperative and the importance of a uniform temperature during extraction is plain. Mr. Veitch raised the question of possible changes in leather at 70° C. and it is known that wet leather may burn above a temperature of 60° C.

Mr. Stacy added a series of results in which the digestion time was three hours at 35° C. and the percolation temperature likewise 35° C. His results are given in Table III-A. This work was under conditions of Mr. Stacy's choosing and as a consequence was not checked by the other Committee members.

TABLE III-A.—PERCENTAGE OF WATER SOLUBLE ON DRY BASIS.

No. of each successive 100 cc. portion	Digestion 3 hours at 35° C. Extraction at 35° C.
1	16.31%
2	2.70
3	1.37
4	1.01
5	0.79
6	0.67
7	0.57
8	0.52
9	0.47
10	0.43
11	0.39
12	0.37
13	0.34
14	0.33
15	0.29
16	0.28
17	0.26
18	0.24
19	0.23
20	0.23
Total	27.80%

Mr. Anthes likewise ran a series of results in which there was no previous digestion and in which the time of extraction was cut to one hour. The results are given in Table IV and were not confirmed. The figures further emphasize the uselessness of a digestion period. From Table II and IV it is considered that the usual three hour period of extraction is quite sufficient.

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TABLE IV.—PERCENTAGE OF WATER SOLUBLE ON DRY BASIS.

No. of each successive 100 cc. portion	Three hours Extraction at 50° C.	One hour Extraction at 50° C.
1	16.22%	14.33%
2	3.75	4.84
3	3.02	2.71
4	1.46	1.29
5	1.08	1.08
6	0.89	0.86
7	0.70	0.72
8	0.61	0.68
9	0.55	0.61
10	0.50	0.54
11	0.43	0.50
12	0.40	0.43
13	0.40	0.40
14	0.35	0.38
15	0.31	0.35
16	0.30	0.32
17	0.26	0.30
18	0.25	0.28
19	0.25	0.25
20	0.24	0.23
Total	31.97%	31.10%

The sixth factor to consider in the water soluble determination is the weight of the sample to be used. Using less than the present amount (30 grams) would be equivalent to an increase in the volume of solvent. From Tables II, III, III-A, and IV and from Tables V and V-A to follow it is in evidence that each succeeding liter of percolate after the first two liters add relatively a small and a decreasing amount to the total extractive. In view of the fact that there is no end point in sight it seems best to retain the two liter percolate as at present and also to retain the thirty gram sample of leather as now.

The seventh and last factor considered deals with the amount of percolate to be collected. Experiments carried on by Messrs. Johnson and Anthes clearly indicate the improbability of extracting all water soluble material. Positive tests with gelatin-salt solution were obtained by Mr. Johnson at the end of three liters, and by Mr. Anthes at the end of two and one-half liters of percolate with ferric chloride solution. Table V gives Mr. Johnson's results and they are self-explanatory and Table V-A gives the

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results of Mr. Anthes which also need no further comment. The seventh factor has been already discussed briefly in considering the amount of leather to be extracted and the discussion there need not be repeated here.

TABLE V.—PERCENTAGE OF WATER SOLUBLE.

Amount collected	Digestion over night Extraction at 50° C.	Digestion 3 hours Extraction at 50° C.	No digestion Extraction at 50° C.	Digestion over night Extraction at 70° C.
1st liter	27.82%	27.26%	27.98%	31.16%
2nd liter	3.56	3.49	3.81	2.93
3rd liter	2.04	2.24	1.78	1.39
Total extractive (3 liters)	33.42%	32.99%	33.57%	35.48%

TABLE V-A.—PERCENTAGE OF WATER SOLUBLE.

Amount collected	Digestion over night Extraction at 50° C.	Digestion 3 hours Extraction at 50° C.	No digestion Extraction at 50° C.	Digestion over night Extraction at 35° C.	Digestion over night Extraction at 70° C.
1st liter	28.78%	28.64%	28.78%	25.18%	34.06%
2nd liter	3.06	3.25	3.19	3.14	2 79
additional ½ liter	0.99	0.88	0.99	1.02	0.80
Total extractive (2½ liters)	32.83%	32.77%	32.96%	29.34%	37.65%

COMMENTS BY COMMITTEE MEMBERS.

MR. S. K. JOHNSON: The results indicate that soaking over night or for three hours does not materially influence the total quantity extracted. At 70° the quantity of water soluble material is increased in the first liter, and there is less in the second and third, though the extraction, even at this temperature, is incomplete, as shown by the gelatin salt test. These results confirm the conclusions of Frey and Clarke (J. A. L. C. A., 1919, Volume 14). In future work on water soluble material it is suggested that the quantity of leather used for extraction be decreased, while the temperature of extraction be raised certainly not above 60° C.

Owing to lack of time, the work called for in Section 4 of the instructions was not done. This point has been covered in the report on Leather Analysis in 1909 (J. A. L. C. A., Volume 4, Page 272).

It is well known that the present A. L. C. A. method does not determine all the water soluble in leather. This fact has been

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shown by numerous data from the Bureau of Chemistry (see reports on Leather Analysis (J. A. L. C. A., Volume 5, Page 426-33, 1910; Volume 6, Page 565-79, 1911); and Frey and Clarke (J. A. L. C. A., Volume 14, 1919)).

I question the advisability of extracting at 70°. While the evidence may not be conclusive, the work on the preparation of samples, which has been reported in the JOURNAL, indicates possible changes in the leather of some of its constituents. Furthermore, it is well known that wet leather may burn at temperature above 60° C. The sample extracted at 70° C. in this work was slightly burnt. It is believed that extraction at 60° would be safe.

MR. R. E. PORTER: Judging merely by one set of results it would seem that it would be best to stick to the present Official Method. However, there is one very desirable and satisfactory feature of extraction at the higher temperature (70°) in so far as in that case the extraction comes to a natural close and is not broken off as abruptly as in all the other extraction.

MR. L. E. STACY: Firstly: The remarkable concordant result of extraction at 50° C.

Secondly: The substantiation of experiments conducted in this laboratory some two years ago — though never published; that no previous soaking is necessary to obtain concordant results where extractions are made at 50° C. This has been the practice in our laboratory for the past two years, with good results.

Thirdly: We observe that the curve plotted for the percentage of extraction at all temperatures used approaches a straight line after the first 1000 cc., which suggests the idea that a concordant result might be obtained by stopping the extraction at this point.

Fourthly: That the confirmation of Mr. Whitemore's hypothesis, with every rise of 5° C. in temperature of extraction there is an approximate increase of 1 per cent. of extractive matter. In comparing the percentage of extraction at 50° and 35°, we note that the converse of this seems to hold true.

We would recommend that the Committee continue this work, paying particular attention to the temperatures less than 50° C., as it is our opinion that a procedure could be worked out at a lower temperature which would give concordant results and would more closely approximate the conditions under which leather is

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ordinarily subjected. The closer the laboratory is to actual practice without the sacrifice of accuracy, the more valuable the results obtained.

This recommendation is in line with the results obtained by Mr. Whitmore, from the analysis of the soles before and after wearing tests, and is also in line with the data in our laboratory obtained by the analysis of leather washed away in the flood of the Yadkin River in July, 1916, which show that this leather after being submerged in river water for a period up to 36 months will still yield water solubles at 50° C.

MR. G. L. TERRASSE AND J. F. ANTHES: The leather before aqueous extraction was completely extracted by petroleum ether and it is suggested that this procedure be made official and not left optional with each analyst.

All aqueous extractions were made in the Churchill-Reed apparatus and it is suggested that this type of apparatus be made official. In view that the extraction was as complete with no period of digestion (31.97 per cent. on dry basis) as with a three hour period of digestion (31.89 per cent.) or an over night digestion (31.84 per cent.) it is suggested that the period of digestion be cut out; provided always the sample is finely ground and ligroin extracted before aqueous extraction.

A pronounced influence of the temperature of aqueous extraction is plain; other conditions equal, extraction at 35° C. gave 28.32 per cent. solubles, at 50° C. 31.84 per cent., and at 70° C. gave 36.85 per cent. Obviously an arbitrary fixation of temperature (say 50° C. as at present) is imperative and the importance of a uniform extraction temperature is plain.

Reducing the total time of extraction to one hour with no digestion period, other conditions equal, reduced the extractive from 31.97 per cent. to 31.10 per cent., thus further emphasizing the uselessness of continued contact of solvent with leather powder. It is hence considered that the three hour period of extraction is ample.

That under any and all conditions the continued addition of solvent adds to the total extractive and it thus becomes necessary to arbitrarily fix the volume of solvent and it is suggested that the 2000 cc. be retained and the amount of dry ligroin extracted leather be fixed at 30 grams.

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All 100 cc. portions under all conditions of extraction gave color reactions with ferric alum.

The hopelessness of anything like an absolute value is evident and for purposes of uniformity between different laboratories the importance of uniform conditions of extractions is self-evident.

Conclusions.

As a result of the work carried out by your Committee we would recommend the following as a basis for the determination of Water Soluble in Leather:

The sample of leather must be finely ground and free from grease.

The extraction is to be carried out in the Reed-Churchill extractor.

Thirty grams of leather shall be used for extraction.

The temperature of extraction shall be 50° C.

Two liters of percolate shall be collected.

There shall be no digestion period and the time of extraction shall be three hours.

Discussion.

Mr. Oberfell: Mr. President, I think we should go very slowly in the adoption of an extraction apparatus under a hydrostatic head, which is the case with the Reed-Churchill extractor. Personally, I am convinced that you get higher results as a result of this pressure, than if you use the ordinary atmospheric pressure. I believe that is confirmed by opinion and the results of some other operators.

Mr. Terrasse: It is extremely difficult for me to conceive an influence by the pressure involved on a question of about two or three inches of water. It is conceivable to me that such an influence may exist but it is pretty difficult to imagine how it would influence the determination of water solubles, which has already extremely varied conditions.

Mr. Orthmann: I made some water soluble determinations not so very long ago with the Koch, the apparatus specified by the Swedish Government, and I found with that apparatus, (which has a reservoir about a meter and a half above the extraction

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flask, giving about a pound and a half pressure) that I secured higher results than with the Churchill apparatus. I found, I believe, that the difference was as high as three per cent. The temperature of the extraction was five degrees lower than our official method, and the time was half an hour shorter.

MR. FREY: I would like to emphasize the fact that the results just given, confirm those published by Mr. Clarke and myself last year in some "Notes on the Determination of Water Solubles." We found, using a large number of samples of sole leather, about twenty in all, that no soaking was necessary; and also that between the range of 45 and about 55° C., we got results which indicated that the rise in water soluble would be about nine-tenths of a per cent. for every five degrees in temperature, which agrees with the results just given.

I am not quite inclined to agree with the statement that three hour extraction is complete enough. I admit that we can hardly hope to get a definite end point, but in the work referred to, we found that in three hours only 85 to 90 per cent. of the soluble matter was extracted, using a 7½ hour extraction under the same conditions as the standard, and even with the 7½ hour extraction all the soluble matter was not taken out.

MR. SCHULTZ: In connection with Mr. Frey's remarks, isn't it a question of what we want to determine here; in determining the water solubles, is it to be for purposes of valuation of the leathers as regards wear, or is it to be for the use of the tanner, for constructive purposes ?

Mr. Alsop made the remark last year, which perhaps was taken as a jest, to the effect that he had heard of people getting into hot water but not walking in it. Analyses of samples of leather that have been used as soles and worn over a considerable period of time in wet weather, shows that there is quite a large amount of water solubles that will still be extracted at 50°. What does the results of the method signify ?

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ORDER OF DIFFUSION OF TANNING EXTRACTS THROUGH GELATIN JELLY AND THEIR RELATION TO RESULTS OBTAINED BY WILSON AND KERN.

By Arthur W. Thomas.

Rec'd Sept. 13, 1920

Recently J. A. Wilson and E. J. Kern[1] have shown that the official method of the American Leather Chemists' Association for the determination of the tannin content of vegetable tanning extracts is in error due to the fact that non-tans are taken up by the hide substance and thus computed as tannins. Those extracts containing the greatest amounts of non-tans give the largest errors by the official method. The errors for various extracts were given by Wilson and Kern as follows:

	Per cent.
Gambier	220
Osage orange	198
Sumac	166
Chestnut wood	117
Larch bark	89
Oak bark	88
Hemlock bark	63
Quebracho	43

or Gambier > Osage orange > Sumac > Chestnut wood > Larch bark > Oak bark > Hemlock bark > Quebracho.

Since tannins react with gelatin to form insoluble compounds while non-tans do not so react with gelatin, it was considered that a comparative measure of the content of non-tans in extracts could be indicated by their diffusion through gelatin jelly, the extent of the diffusion being measured by the formation of a black color which many of the non-tans produce when treated with ferric ion. The diffusion of tannins through the jelly would in any case be extremely slow compared with the diffusion of non-tans due to the high molecular weight of the former in comparison to the latter.

A 5 per cent. dispersion of gelatin in hot water containing 0.1 per cent. ferric chloride was poured into a series of test tubes to three-quarters of their capacity. When the gelatin dispersions

[1] *J. Ind. Eng. Chem.*, **12**, 465 (1920).
This Jour., **15**, 295 (1920).

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had set to jelly, equal volumes of solutions of different extracts were placed on top of the jellies and set in an ice-box. The extracts were all made up to 1 per cent. concentration on the basis of the total dry solids which they contained.

At the ends of certain intervals of time the diffusions of the non-tans, as shown by the black zones, were measured. Duplicate tests were performed in each case and the averages of the results are noted below.

DIFFUSION OF NON-TANS THROUGH GELATIN JELLY.

Material	48 hours	96 hours	144 hours	216 hours
Sumac	17.3 mm.	22.3 mm.	27.0 mm.	32.5 mm.
Gambier	13.8	18.0	22.0	26.0
Chestnut wood	12.0	17.8	20.0	23.8
Oak bark	9.0	13.0	15.2	18.3
Larch bark	9.0	12.0	14.5	16.0
Hemlock bark	6.0	8.3	9.5	12.0
Osage orange	4.3	4.8	5.0	6.0
Quebracho	3.8	4.8	5.8	7.3

The order of diffusion of the non-tans was, therefore—
Sumac > Gambier > Chestnut wood > Oak bark > Larch bark > Hemlock bark > Quebracho > Osage orange.

With the exception of Osage orange, the order found here is similar to the order given by Wilson and Kern. The discrepancy in the position of Osage orange is due to the fact that this material contains very little non-tans which react with ferric ion to produce a black color, but it does contain a large amount of non-tan in the form of a yellow dye-stuff which does not react with ferric ion. The similarity of the order to that obtained by Wilson and Kern is very significant, especially since the samples of extracts used were not identical with those used by Wilson and Kern.[2]

A similar experiment was performed by A. W. Hoppenstedt[3] in which he used extracts of such concentrations to contain 4

[2] NOTE.—We fail to see any significance in the similarity to the results obtained by Wilson and Kern. The rate of diffusion as measured here is simply a function of the non-tannin content, and is dependent upon the nature as well as the concentration of non-tans. The order of increasing rate of diffusion as found by Dr. Thomas is, in general, the order of increasing non-tannin content by the official method, with chestnut extract out of place.—ED.

[3] This JOUR., 6, 343 (1911).

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grams of tannin per liter, as determined by the official method. The order of diffusion which he found was—
Sumac > Divi-divi > Gambier > Chestnut extract > Myrobalans > Oak extract > Valonia > Algarobilla > Hemlock bark > Quebracho extract > Mangrove bark.

I take pleasure in acknowledging the generous support of Messrs. A. F. Gallun & Sons Co., in this work.

COLUMBIA UNIVERSITY,
New York City.

THE ANALYSIS OF SULPHONATED OILS.*

It is the opinion of the chairman that a difference of 1 per cent. more or less from the actual content of total fatty matter and a difference of 2 per cent. more or less for neutral fat is not very material in the valuation of a sulphonated oil and therefore would recommend that total fatty matter in a pure oil be determined as the difference between 100 and the sum of moisture, ash, unsaponifiable, ammonia and combined SO_3. From the saponification value of the sample and this value for total fat, the saponification value of the fat can be calculated and this value may be used to calculate the neutral fat after deducting the value for combined and free fatty acid from the saponification value of the sample.

The chairman recommends that the analysis of sulphonated oils contain the following determinations:

(1) Moisture, Ash, Unsaponifiable, Combined SO_3, Ammonia and Total Fatty Matter.

(2) Total Alkali and Free Fatty Acids (expressed in milligrams of KOH per gram) and Neutral Fat (optional). The chairman suggests that the following procedures be recommended for adoption as official methods of the Association:

Moisture.—The Xylol method as given in the provisional methods and as alternative the method as recommended by the committee for 1917, this JOUR. **12**, 276 (1917).

Ash.—The determination as given in the provisional methods.

Unsaponifiable.—The method as given in the committee report for 1919 under method B, this JOUR. **14**, 268 (1919).

* Discussion following the presentation of the 1920 Committee report at Atlantic City, May 28, 1920.

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Combined SO_3 and Total Alkali.—As given in this report under method A, page 283, however, making the total alkali determination read: Weigh 10 grams into a 250 cc. Erlenmeyer, dissolve in 150 cc. water (warm if necessary to effect solution), add 30 grams granulated salt, 25 cc. ether and 5 cc. of methyl orange indicator and titrate with N/2 H_2SO_4. The method for combined SO_3 as given under method B be adopted as alternate method.

Ammonia and Free Fatty Acids.—As given under method A in the 1919 committee report, this JOUR. **14**, 267 (1919).

Total Fatty Matter.—To be taken as the difference between 100 and the sum of moisture, ash, unsaponifiable, ammonia and combined SO_3 as determined above.

Neutral Fat.—Determine the saponification value of the sample as given in this report, page 286, and calculate to sap. val. of fat by dividing by the weight of total fatty matter. From the sap. val. of the sample subtract the combined values of total alkali and free fatty acids and divide the remainder by the sap. val. of fat. This result multiplied by 100 is equal to the per cent. of neutral fat.

DR. C. G. BUMCKE: The results for combined SO_3 by the Hart method are really so surprisingly good, (there is only a difference of one or two-tenths of a per cent.) that I don't see any objection to adopting this method at least as optional beside our old Method B.

The only thing here that looks somewhat peculiar to me, and I think gives a cause for a wrong interpretation of the analysis, is the statement of the amount of total alkali as KOH. We never have KOH in sulphonated oils, and we chemists understand very well what it means if we give it that way, but I think the expression comes nearer to what we really have in our samples, when we express that either as NaOH or Na_2O. This is at least a point that we could take into consideration.

The results for combined SO_3 by Method A, are always a little lower than by Method B, and Mr. Cuthbert here says, "In a similar manner the results for Combined SO_3 obtained under Method B are usually somewhat lower than the results obtained by ashing the oil with Na_2CO_3 and determining the SO_3 gravimetrically as suggested by W. K. Alsop a few years ago." Now

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before we do anything there, I want to sound a warning against the adoption of this method. By ashing the oil, we get all the sulphur that is present turned into SO_3, and as oil sometimes contains some sulphur naturally, this would appear as combined SO_3, too. But there is another danger — which is demonstrated by a recent occurrance in our laboratory. We received a sample that we suspected to be a sulphonated oil, and examined it by the ashing method, and found a considerable amount of combined SO_3, but hardly no inorganic SO_3. However, the values that we got for total alkali and free fatty acids were so low, that we couldn't bring this into accord with the high figure of combined SO_3. We then tested the sample according to Method B and found no combined SO_3. This showed plainly that we had to do with a sulphur oil and not with a sulphonated oil. The method itself is all right for factory control, where you know you have a sulphonated oil, but when you have an unknown sample, it is not safe to apply that method.

For the testing of Samples 4 and 5, both Method A and B for total fat are always too low, because they are based on a saponification value which we get after we dry the oil. If we want to obtain accurate results, we must apply another method; that is, by weighing the fatty acids as soap when the danger of loss on drying of the volatile acids is eliminated.

Neutral fat, by all methods, was always found too high. This is just the opposite to what should occur; if the saponification value of the sample were somewhat smaller, the amount of neutral fat would be still greater, and therefore I want to ask Mr. Schultz whether he determined in the oleic acid the unsaponifiable or whether he figured the whole oleic acid as oleic acid ? The commercial product, as you know, contains a good bit of unsaponifiable; 3 to 4 per cent.

Mr Schultz: The unsaponifiable together with the saponification, and acid values of the oleic acid employed was determined and it was something like three-tenths of one per cent. which was not taken into consideration.

Dr. Bumcke: Then we really have here something that lacks explanation. It is very peculiar that no matter what method we apply, we always get much higher; that is, from four to seven and a half per cent. higher than the figure actually should be.

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It was proposed by the Chairman to adopt as total fatty matter, in order to get away from these errors that I just mentioned, the difference between 100 and the sum of moisture, ash, unsaponifiable, ammonia and combined SO_3. I don't think that it is safe to do this. For instance, if we have an oil that contains five per cent. of Combined SO_3 and perhaps eight per cent. of ash, we would deduct those thirteen per cent. from 100, while the organic SO_3 is really contained in this eight per cent. ash. Consequently, our amount of total fatty matter would come out five per cent. too low, or five per cent. lower than it actually was. For that reason I don't think we can call the difference between 100 and these different items the total fat.

On page 294, under Number 2, the total alkali and free fatty acids expressed in milligrams of KOH per gram, should be determined as here represented. I think it should be called "Actual Acids," because that is what it really is.

In conclusion, I want to call your attention to the determination of neutral fat, on page 287; for the extraction with petrol ether, we must dilute our alcohol. I think that has been omitted. There is a misprint in my comments, page 292, line 25, "In method B, neutral fat No. 1, the dilution of the alcohol to about 50 per cent. for the petrol ether extraction was omitted," should read "should not be omitted."

MR. SCHULTZ: In using mmg. KOH per gram as the values for total alkali and free fatty acids it is simply used as a convenient term in designating different values for fats and oils, and we do so here for the sake of conformity and convenience in calculating the results.

As for ashing with sodium carbonate, to determine the total sulphur, as Dr. Bumcke mentions, the remark made by Mr. Cuthbert is not valid and this procedure has been ignored by the past several committees on this account.

As to the statement that the high results for neutral fat lack explanation, I have offered a plausible explanation for the results by method A in the use of the mean molecular weight (see page 288).

The question that Dr. Bumcke raises with reference to the determination of the total fat by difference, is worthy of consideration. In adopting that method, we were simply choosing what appeared to be the lesser of two evils.

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Mr. Hart had some remarks to make on the question, shortly before he left, which was the only objection he could find to the method as outlined, namely, the possibility of adding the SO_3 twice, which in some cases may cause considerable error. However, after suggesting that this may be corrected by a simple calculation from the values already determined with method A he was satisfied that the outlined method, as proposed, would be quantitative and satisfactory.[1]

DR. BUMCKE: As to determining the total fatty matter by difference, there is another fact I forgot to mention. There are some sulphonated oils that have a little alcohol in them. How about that? That would be given as total fatty matter, too.

MR. SCHULTZ: We may assume any number of conditions that may obtain in sulphonated oil; there may be also petroleum ether present; there may be kerosene, any unsaponifiable oil that will volatilize on evaporation. I think it is up to the chemist to exercise his judgment in such a case, if he gets results that do not appear exactly right. If there is alcohol present, the moisture determination can be modified or we can adopt any method that would be convenient for its determination. But as for outlining methods that will cover every possibility that may obtain, it would be rather a lengthy and stupendous method or system of analysis.

NOTE.—The recommendations of the chairman were republished here with the discussion on the request of the Council, for consideration by the active members. Criticisms and comments both constructive and otherwise are invited so that the committee may continue its work if need be. Otherwise these recommendations are to be altered to conform with Hart's proposal for the determination of total fat by difference and submitted for adoption as official methods. Address all correspondence to G. W. Schultz, % Elk Tanning Co., Ridgway, Pa.

[1] Mr. Hart has recently published two papers which cover this point entirely. This JOUR., 15, 404 and 495 (1920).

ABSTRACTS.

Leather Measuring Machines. By F. J. SCHLINK, *Bureau of Standards Technologic Paper* No. 153. An investigation of the several types of leather measuring machines is described in detail, the principles of construction and the source of error given. The pin machine, now no longer made, has several advantages in simplicity of construction, low cost of manufacture and satisfactory accuracy when sufficient pin elements are used. Of the alleged disadvantages of low speed of operation and of

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failure to account for the area involved in the concavity of the hide, the author believes that the first are overdrawn. The sources of error of the more generally used power-driven wheel machine and possibilities of minimizing the same are taken up under the respective items of spacing of wheels, width of wheel rim, overrun of wheel work, imperfections of link work and variations in thickness of the leather. Under the first two headings the influence of the shape and outline of the skins is clearly shown, while the importance of control of speed of operation is brought out in the discussion of overrun of wheel work. Of the above five major sources of error each of the first three tends to give readings greater than the true area while the last two may influence the result either way. Methods for testing and calibrating the machines and for determining machine performance are discussed. Several materials for test standards and suitable outlines for standard patterns are under consideration, it having been shown that the use of rectangular test sheets has resulted in the acceptance by weights-and-measures authorities of apparently satisfactory machines which when later used on hides and skins, with their irregular outline, were subject to very large error. C. A.

Effects of Oils, Greases, and Degree of Tannage on the Physical Properties of Russet Harness Leather. By R. C. BOWKER and J. B. CHURCHILL, *Bureau of Standards, Technologic Paper No. 160.* The effect of different amounts of stuffing content, of mineral and animal oils and of medium and heavy tannage on the physical properties of russet harness was investigated and it was found that the amount of stuffing content affects the tensile strength of the leather and that there is a point beyond which the amount of stuffing content used does not add to the strength and may actually decrease it; that the tensile strength is greater for leather tanned a short time than for leather given a long time tannage, and that the degree of tannage also affects the firmness of the leather, the longer-time tannage producing leather more resistant to shear when used with a buckle; that mineral oil of the type used does not affect the physical properties of new leather in a manner different than cod oil.

The variation in tensile strength, stretch and buckle strength in leather from different parts of the hide is given for the six sides of leather investigated.

New Filters. By KARL SCHORLEMMER, *Collegium*, 1919, No. 586, pp. 46-50. Zsigmondy and Bachmann (*Zeit. f. angew. Chem.*, 1918 [103]) define the action of ordinary filtering material as mainly that of a sieve; this action can be modified by adsorption whereby particles smaller than the sieve opening may adhere to or penetrate the filter substance. This is notably the case with filters of porous earthenware. A fully reliable filter then should act only as a sieve; the fine pore ultra-filters of Bechhold and others belong to this type. Z. & B. have succeeded in making from certain colloids a filter having the advantages of the ultra-filters and suitable for technical use. E. de Haën, Chem. Fabr. "List" manufacture these so-

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called "membrane filters." They are furnished in various grades of porosity designated by three or four place numbers. The first figure is a factory mark, the following two (or three) represent degree of fineness. Thus Nos. 315 and 915 are coarser than No. 330. Filters of coarser porosity (x01 - x15) hold back nearly all visible turbidities; medium filters (x15 - x35) arrest particles down to 1/10,000 mm. diameter and are specially suited for filtration of bacteria. The filtration apparatus consists of a suction funnel with a ground rim, a porcelain perforated plate or a porous ceramic plate to support the membrance filter and an upper ring to hold the liquid for filtration. The joints between funnel, plate and reservoir ring are packed with rubber, asbestos or paraffin paper and the whole clamped together by screws. When a perforated plate is used, a layer of filter paper is placed beneath the membrane filter in order that the entire surface may filter and not merely over the holes. One surface of the membrane filter is smooth and glazed; this is placed upwards and enables a ppt. to be removed quantitatively.

The writer reports some preliminary trials of these filters with tanning solutions. A mixture of oak and pine-bark extract was used. This gave with an extra hard S. & S. 602 filter 4.65, 4.53 per cent. insolubles; with a membrane filter 306 the same sol. gave 10.93 per cent. This shows that the coarse grade (306) is still too fine for tannin analysis. Further trials with coarser filters are desirable. As the inventor claims these membrane filters can be produced in great variety of specified thickness and porosity, it may be hoped that a suitable filter could be furnished for tan-stuff analysis giving more dependable results than usually obtained. A single trial of using again the 306 membrane filter after cleaning and drying, gave the same result as the first time. W. J. K.

Effects of Cold upon Raw Hides and Skins. *Ledertechn Rundschau,* 1915, 44, through *Collegium,* 1919 No. 587, p. 87. Cold, while preserving hide, also injures it by freezing, the ice crystals rupture the tissue. A thawed hide is of soft texture, without resistance and yields a leather which is without firmness or durability. Such leather lacks strength and is useless for belting or anything involving stretching or high pressure. That a hide has been frozen cannot be recognized by appearance; a loose feel may be due to other causes. It is therefore important that unsalted hides be not exposed to frost; the danger is less when salt is used. It is an error to assume that cold cannot injure hide substance. W. J. K.

Determination of Sulphuric Acid. L. W. WINKLER, *Zeit. f. Angew. Chem.,* 1917, [30, I.] 251, through *Collegium,* 1919, No. 587, p. 95. It is of consequence in pptg. $BaSO_4$ whether the sol. be neutral, weak acid or strong acid; in acid sol. the ppt. contains Ba-hydrosulphate.

1. Neutral Soln; this is heated to boiling, $BaCl_2$ added drop by drop in moderate excess giving pure, moist $BaSO_4$.

a. The precipitate is collected on paper, washed, dried and ignited; residue moistened with 1-2 drops H_2SO_4 and again ignited.

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b. Weighing the dried precipitate gives more accurate results: the precipitate is collected on a cotton pad, washed and dried at 132°; for computation, the weight is reduced by 0.68 per cent. It is still more accurate to transfer the greater amount of the dried precipitate to a platinum crucible and determine the ignition loss direct.

2. In weak acid solution; 100 cc. neutral solution are acidified with 2.25 cc. N/10 HCl and precipitate according to (1); precipitate collected on cotton dried at 132°, computed as pure. This is the easiest method for an accurate (to 0.1 per cent.) determination of H_2SO_4.

3. In strong acid solution; 5 cc. N.HCl are added to 100 cc. assay solution which is then precipitated by (1), collected on paper, washed and dried at 132°; 0.46 per cent. is added to weight; if ignited, 0.86 per cent.

4. In 10 per cent. HCl; after precipitation in hot solution, the liquid is evaporated, precipitate leached, then collected on a filter, ignited and weight increased by 1.5 per cent.

Methods (1), (2) recommended for solutions containing NH_4, K, Na and Mg sulphates, chlorides and borates; method (3) in presence of Zn, Cd, Mn, Cu, Hg, Al, Fe(ous), Co or Ni; method (4) in presence of Ca, Cr or P_2O_5. W. J. K.

Determination of Chromic and Polychromic Acids. L. W. WINKLER, *Zeit. f. Angew, Chem.*, 1918, [31,I.] **46**, through *Collegium*, 1919, No. 587, p. 96. I. As $BaCrO_4$; the solution should contain but a slight amount of acetic acid, else the separation is incomplete, even with great excess of reagent; NaCl is added to secure a granular instead of a fine precipitate. To 100 cc. of the neutral, alkaline chromate solution of about 0.2 per cent. content, 1 cc. N/10 acetic acid is added, then 1 g. NaCl, all heated to boiling and 5 cc. "10 per cent." $BaCl_2$ solution added in drops; gentle boiling maintained 2-3 minutes. Next day the precipitate is collected on padded cotton, washed with 50 cc. cold H_2O, dried 2-3 hours at 132°. For large amounts, pump is used. Precipitate dried at 132° loses 0.25 per cent.

Chlorides of NH_4, K, Na, Mg, Ca have no effect on the result, but nitrates, chlorates and acetates increase the weight of precipitate. To determine pyrochromate, a little sulphate free precipitated $CaCO_3$ is added to the solution of about 50 cc. which is then boiled 10 minutes. After several hours, the pure yellow solution is filtered and rinsed to 100 cc. solution which is then precipitated as above.

II. As Ag_2CrO_4 (in presence of sulphates); 100 cc. of the neutral, about 2 per cent. alkaline chromate are heated to boiling and 5 cc. 10 per cent. $AgNO_3$ added with shaking. This is left stand over night, then filtered through cotton and washed with 50 cc. saturated solution $AgCrO_4$; precipitate dried at 132°; all operation in artificial light. The results are accurate, but if pure H_2O be used for washing, too low. The presence of foreign salts has little influence. When H_2SO_4 is present, the precipitate contains some Ag_2SO_4 which cannot be washed out. The following table of corrections in milligrams applies to 100 cc. solution precipitated as above.

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Grams dry ppt.	Grams SO_4 in 100 cc. 0.5	0.4	0.3	0.2	0.1
0.30	7.0	6.1	5.2	4.1	2.7
0.25	5.6	5.0	4.3	3.4	2.1
0.20	4.5	4.0	3.5	2.7	1.6
0.15	3.5	3.2	2.8	2.1	1.2
0.10	2.7	2.4	2.1	1.6	0.9
0.05	2.0	1.8	1.5	1.2	0.6
0.03	1.6	1.4	1.2	1.0	0.5

Pyrochromates are first converted into chromates with $CaCO_3$; NaCl or acetic acid are not added. W. J. K.

Corinal, a New Synthetic Tan-Stuff. By WALTER BUCKOW, *Collegium*, 1919, No. 591, pp. 211-15. This substance has been earlier described by Paessler; its manufacture has now been improved by the Chemische Fabrik Worms and the material is being introduced in the market. The author reports an examination (Laboratory of Leather Industry, Maschke, Berlin) made in behalf of the manufacturer.

Corinal is a clear, dark brown liquid, specific gravity 1.306, mixing clear with cold H_2O, but turbid, and considerable precipitate with hot. Reaction acid, but neutral to Congo, no mineral acid; greenish black reaction with Fe salts; strong Proctor-Hirst reaction. With chromed hide-powder (filter method):

	Hot solution	Cold solution
Tans	26.7	33.6
Soluble non-tans	15.8	17.9
Insoluble	8.9	0.2

Mineral content, 12.88 per cent., including Al_2O_3 5.87, CaO 0.14, Mg salts 0.09.

To test the tanning power, powdered, previously limed hide-powder was drummed with Corinal solution 4 times, ½ hour each, whereby 30 per cent. of the tans and 2.7 of the non-tans were taken up. Further, limed calf hide was separately treated in suspenders as well as in drums for 6 days with 5 per cent liquors from Corinal, oakwood extract and valonea extract; all gave good, full leather, tanned through, the Corinal being more rapid in action. The germicidal action was tested by adding Corinal to 10 per cent. oak- and pine-bark extracts which alone developed marked mold after a week. The addition of 0.25 per cent. retarded and 0.5 per cent. prevented molding after 2 weeks; pine-bark was retarded easiest. Additional general tests with new samples of Corinal gave similar results; the leather produced was of uniform color, faultless grain, without brittleness. A sample of Corinal tanned leather from the manufacturer gave 4.00 per cent. mineral including 2.13 Al_2O_3; a sample from mixed Corinal vegetable tannage gave 2.79 including 1.04 Al_2O_3. The Al in the Corinal becomes fixed with the hide; the spent liquor contains mere traces. Corinal undiluted does not injure hide; the material may be rated as a good tanning agent. W. J. K.

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Tannins from Wattle Bark. By W. McGLYNN, F. A. COOMBS, et al., *Commonwealth of Australia, Science & Industry*, 2. 150 (1920). For many years the bark used in Australian tanneries has been obtained mainly from two species of wattle, the golden wattle (*Acacia pycnantha*) and the black or green wattle (*Acacia decurreus*) and its varieties. The Australian supply has become inadequate and has been largely supplemented by wattle bark imported from Natal, where plantations have been formed by the utilization of Australian seed. A valuable tan bark is yielded by the mallet (*Eucalyptus occidentalis*) of Western Australia; although it was only discovered in 1903 its exploitation was so rapid that only small quantities now remain.

To insure a local supply of tannin for the future, four possible means have been suggested: (*a*) Regulation of bark collecting to prevent the destruction of young trees; (*b*) plantation of wattles for the production of bark; (*c*) discovery of new sources of tannin; (*d*) manufacture of tannin extracts.

This investigation by a committee of the Commonwealth Institute of Science and Industry had for its primary object, a more efficient method for extracting wattle bark for use at Australian tanneries. These tanneries require strong liquors and the research was conducted with this end in view. For the experimental work a battery of six jacketed copper vats was used, the capacity of each vat was 5,250 cc. The bark used was ordinary coarse ground Adelaide bark (*Acacia pycnantha*) as supplied to tanners and gave the following results on analysis:

	Per cent.
Tannin	37.55
Non-tannins	10.68
Insolubles	40.17
Water	11.60
Total	100.00

The water required to cover the dry bark in each vat was from 4,000 to 4,500 cc. and 2,600 cc. were drawn off each day. The experiments were conducted on the "press leach system" as this was considered the best for extracting bark at tanneries. Spent bark was removed and replaced by fresh bark each day (except Sunday) thus each charge remained in the battery for a period of seven days. The table below gives the results of the experiment.

Experiment number	Temperature of tail leaches °C.	Tannin extracted Per cent.	Tannin in spent bark Per cent.	Tannin lost Per cent.
1	20–25	64.10	31.10	4.80
8	35	74.35	22.90	2.75
7	40	74.10	21.70	4.20
6	60	79.48	18.30	2.22
5	80	84.82	11.54	3.64
4	90	90.80	5.56	3.64
3	90	90.60	5.59	3.81

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The paper is concluded with the following summary:

1. Spent wattle barks, taken from various tanneries in New South Wales, contain considerable amounts of tannin, and these undesirable results can be attributed to the faulty methods adopted for the extraction of tannins.

2. Satisfactory results are not always obtained by tanners who grind their own bark. A mill is not doing good work when it allows any large particles of bark to pass through without being crushed. The ground Adelaide bark used for the experiments described in this paper may be cited as a good example of how bark should be prepared for the extraction vats.

3. The additional cost of grinding, the mechanical agitators required, and the resulting cloudy liquors, are factors which adversely affect the use of bark in the powdered state.

4. For all practical purposes the maximum for a "one liquor period" when water is added to the wattle bark is not above twenty-four hours, and this period decreases as the temperature increases.

5. An open diffusion and continuous process, worked on the press leach system appears to be the most useful for the extraction of tannin from wattle bark.

6. Eight vats are recommended for a press leach system battery working under normal conditions; but when the bark swells to such an extent that percolation is retarded, then nine vats are recommended. By this means the tanner can shift the bark once during the process of extraction.

7. The amount of tannin destroyed, or the difference between the total tannin and the sum of the tannins in solution and in the spent bark, is apparently low for wattle bark.

8. If the percentage of tannin extracted from a bark were a constant quantity, then the tannin concentration of the liquor drawn off each day would be inversely proportional to its volume, but one would expect that the percentage of tannin extracted from the bark would decrease as the volume of liquor drawn off each day decreased. Within the limits of the experimental work described here, it is considered that the minimum volume of liquor to be drawn off each day should be approximately equal to the amount of weak liquor that could be drawn off the bark in one pit.

9. The maximum volume of liquor that can be drawn off the bark each day will depend on the strength or tannin concentration of the strongest liquor required in the tannery.

10. High temperatures (80° C. to 100° C., or 176° F. to 212° F.) are necessary before it is possible to extract a high percentage of tannin from wattle bark.

11. Many tanners fail to get good results because they do not pass sufficient water at a high temperature through the bark.

12. Under the conditions described for these experiments, at least three vats must be raised to the high temperatures before sufficient hot

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liquor will pass through the bark to remove a good percentage of the tannin.

13. As the volume of liquor drawn off each day increases, the number of vats to be maintained at a high temperature decreases.

14. From an economic standpoint, the best extraction results will be obtained when the process is worked on a large scale, and one good extraction plant in the various Australian tanning centres could be expected to supply tannin in solution at a much cheaper rate than when each tanner treats his own bark.

In submitting the above results, the committee felt justified in recommending the extraction process of the press leach system for wattle bark to the favorable consideration of those interested in the tanning industry, as it is considered that this process would be found more advantageous and efficacious than the method generally employed in Australian tanneries.

G. W. S.

On the Value of Planting Chestnut. *Ledertechn. Rund.*, 12. 75 (1920). Before the war only the wood of the chestnut ("Edelkastanie," *Castanea vesca Gaertn.*) was used for the production of tanning extracts, which were produced in France and Italy and imported into Germany in considerable quantities. This chestnut exists in considerable quantities in Germany and when the scarcity of tanning materials during the war forced attention to the domestic supplies, it was used in considerable quantities. Paessler called attention to the fact that the bark contained tannin as well as the wood, and found that at an age of 15-25 years will yield 4-7 times as much tannin as oak of the same age from oak plantations. It was therefore recommended that chestnut be planted in plantations, favorable to its growth, as the oak was removed. The Central Union of the German Leather Industry suggest that more attention be devoted to the planting of chestnut not as a substitute or by displacement of the valued oak but as a means of increasing domestic tannin production.

G. W. S.

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CONTENTS

Dyers Formulae - - - - - - - - 607
Hide Substance. By G. L. Terrasse - - - - - 608
Committee on Limeyard Control, II. The Analysis of Lime Liquors. By W. R. Atkin and W. E. Palmer - - - - - 620
Abstracts - - - - - - - - - 629
Patents - - - - - - - - - 646

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G. W. SCHULTZ . . . . . Associate Editor

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DYERS FORMULAE.

We have received from the National Aniline & Chemical Company, Inc., a twenty-four page pamphlet of convenient size entitled Dyer's Formulae. This is particularly for use in connection with the Spring Season's shade card issued by the Textile Color Card Association of the United States, Inc.

The shades of particular interest to leather men are ten in number given on pages 23 and 24, and it will be a source of convenience to have at hand the information that will aid the

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colorer to proceed at once with his work when called upon to match any one of the shades given, since the preliminary laboratory work is already completed.

Copies may be obtained without cost from any of the offices of the Company.

HIDE SUBSTANCE.*

By G. L. Terrasse.

Every tanner has at least one thing in common with every other tanner, namely, his need of something to tan. That something in ninety-five or more per cent. of the cases is the skin of some terrestrial mammal. In a few per cent. of the cases skins from various amphibia, fishes, lizards, snakes, etc., are tanned; but from the tanner's view-point these are not type skins but specially modified natural classes which served certain out of the ordinary needs of their erstwhile possessors while alive. We will confine our consideration of "hide substance" exclusively to the outer envelope of that large class of mammalia which lives largely or wholly on land. Very much of the hide dealer's and tanner's knowledge of skin comes from the domain of human anatomy, for the human covering differs structurally but little from the animal skins of trade.

We can never lose sight of the fact that before the tanner gets his skin it was part of a living organism and in that word "living" all knowledge of to-day is still Stygian darkness; for how long, who dares say? As once part of a living creature a skin had its functions. Among these it was the seat of the sense of touch and the thermal sense; in its structure are certain organs of secretion and excretion; it may be an organ of absorption; and even while still alive on the animal it was an organ of protection. The tanner and shoemaker have utilized the last feature in ministering to the needs and pleasures of man.

A microscopic inspection of a skin gives us merely some rough notions as to hairiness, thickness, color, furrowings and so on of the hide. A microscopic investigation at once shows an enormously complex structure and in this address the embryonic mor-

* Delivered at the Atlantic City Meeting of the A. L. C. A., May 28, 1920.

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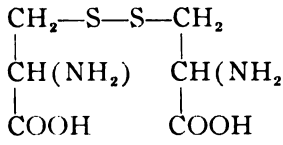
phology cannot be considered and the skin complex is here taken as a finished anatomical organ.

If a cross section of a skin be microscopically examined the outermost layer constitutes the epidermis or cuticle or scarf skin. The outer surface of the epidermis is made up largely of flattened cells, the so-called squamous or pavement epithelium. This epidermal layer is usually regarded as completely lost in beam house work although this is not always the case. This epidermal tissue in its modified forms constitutes the main structure of hair, callouses, nails, horns, hoofs, and similar tissues. If from this list of anatomical units we exclude the nails and horns, and add epithelial tissue we have a group of beam house raw products which at least have one common property, namely, producing together with others the degradation product keratin, or better keratins. This poorly defined albuminoid is best chemically described as being insoluble in water, weak acids and weak alkalies, and as having a relatively high sulphur content. It gives the xanthoproteic reaction (turning yellow with strong nitric acid) and reacts with Millon's reagent (turning red on heating with mercuric nitrate and nitrous acid).

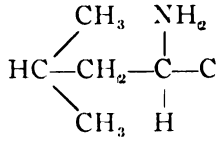
Cystine has however been made from the keratins and its constitution is well known. Cystine is α-diamino—β-dithio-dilactylic acid or better di (β-thio—α-amino-propionic acid).



(Cystine).

This acid is an aliphatic, alpha di-amino, di-carboxylic acid; has two asymetric carbon atoms, hence is optically active (levo); and is amphoteric (both base and acid in character). The ability to assign a specific formula to a decomposition product of a part of a hide adds to our beam house knowledge.

Leucine occurs also in rather large amounts as a cleavage product of the keratins and is α-amino-isobutyl-acetic acid:



(Leucine).

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Leucine is thus an mono-amino, mono-carboxylic acid, optically active (levo); is amphoteric, and has a bitter taste.

The following are also degradation products of the keratins and they are given in alphabetical order; first the common name, and then the chemical name and structural formula.

Alanine:—α-amino-propionic acid—$CH_3.CH.NH_2 . COOH$.

A mono-amino, mono-carboxylic, levo acid; is amphoteric and sweet in taste.

Aminovaleric Acid:—α-amino-iso-valeric acid—

$$\begin{matrix} CH_3 \\ \diagdown \\ CH_3.CH.CH.NH_2.COOH. \end{matrix}$$

A mono-amino, mono-carboxylic, dextro acid; is amphoteric and of sweet taste.

Arginine:—δ-guanidine-α-amino-valeric acid—

$$\begin{matrix} HN \\ \diagdown \\ H_2NCHNCH_2.CH_2.CH_2.CH.NH_2.COOH. \end{matrix}$$

A di-amino, strongly basic, mono-carboxylic, dextro, amphoteric acid.

Aspartic Acid:—amino succinic acid—

$$CH_2.COOH . CH.NH_2.COOH.$$

A mono-amino, di-carboxylic, amphoteric, levo acid.

Glutamic Acid:—α-amino-normal-glutaric acid—

$$CH_2.COOH.CH_2.CH.NH_2.COOH.$$

A mono-amino, di-carboxylic, dextro, amphoteric acid.

Glycocoll:—amino acetic acid—$CH_2.NH_2.COOH$.

A mono-amino, mono-carboxylic, inactive acid.

Phenylalanine:—β-phenyl-α-amino-propionic acid—

$$C_6H_5.CH_2.CH.NH_2.COOH.$$

A mono-amino, mono-carboxylic levo, amphoteric acid.

Proline:—α-pyrrolidine-carboxylic acid—

$$\begin{matrix} H_2C & \text{———} & CH_2 \\ | & & | \\ H_2C & & CH.COOH. \\ & \diagdown\ NH\ \diagup & \end{matrix}$$

A levo, mono-carboxylic, amphoteric pyrrol derivative.

Serine:—α-amino-β-hydroxy-propionic acid—

$$CH_2.OH.CH.NH_2.COOH.$$

A mono-amino, mono-carboxylic, mono-hydroxy, levo, amphoteric acid.

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Tyrosine :—α-amino-β-para-hydroxy-phenyl-propionic acid—
$C_6H_4OH.CH_2.CH.NH_2.COOH.$

A mono-amino, mono-carboxylic, levo, amphoteric acid.

It is from comparisons of similar ideas and substances that the sum of our knowledge is extended, and a comparative study of the twelve cleavage products of the keratins just enumerated, may next be considered.

Nine of these twelve well defined substances are mono-carboxylic acids; that is each one of the nine has one COOH group. The three remaining members of the twelve have two COOH groups each. They are hence capable of functioning as simple mono or di-basic organic acids when brought into contact with univalent basic radicals under certain conditions. No keratin cleavage molecule containing more than two carboxyl groups seems as yet to have been separated and identified. These acids are not strong acids in the ordinary sense, and their dissociation into hydrion and cation is probably small, although but few, if any, electro-chemical measurements in this regard appear to have been made. In certain ones of the twelve fission products the acid character is over-shadowed by the basic amino and imino nitrogen.

Of these twelve carboxylic acids nine have one amino (NH_2) group and this group is always in the α position. The reasons for the alpha grouping of the NH_2 and COOH groups must be looked for in the keratin complex, although in the case of amino acetic acid there is only one position possible for the amino group. Cystine is in a sense the only di-amino acid among the twelve, each NH_2 group being contiguous to one COOH group; and hence there are two alpha amino groups in cystine. Arginine, the other di-amino cleavage product of the twelve listed has one NH_2 group in the α position and the other NH_2 group is part of a guanidine residue, said residue also containing the imino group (NH). Proline, the last of the twelve, has no amino group but an imino group in the pyrrol ring and this NH group is also in the α position. In every acid at least one N atom with its two or one hydrogen atoms occupies an alpha position.

The presence of at least one amino or imino group in each of these twelve carboxylic acids gives these their amphoteric nature; thus enabling each basic nitrogen atom to add to itself other acids,

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the valence of the nitrogen passing from three to five. It must be recalled that the basic character of these amino acids is not pronounced. In arginine with its three basic nitrogen atoms in each molecule the basic character is stronger than in the others. The basic portion of each one of these amino acids doubtless tends to reduce the influence of the acid portion of these amino bodies, making these amino acids susceptible to external chemical influences of other bases and acids.

Nine (by far the largest percentage) of these twelve amino acids have aliphatic nuclei, or, in other words, are open chain molecules. The significance of this feature in regard to the keratins is obscure. A consideration of this feature is still further complicated when it is recalled that two of these twelve have carbo-cyclic nuclei, and one, proline, has a heterocyclic ring containing nitrogen, a pyrrol ring in fact.

The keratins on cleavage incline to the formation of mono-carboxy acids, and mono-amino acids in larger amounts as opposed to the formation of di-carboxy acids and di-amino acids. This follows from the formation of leucine and cystine in largest amounts on keratin degradation. Cystine is probably better considered as being made up of two thio-amino-propionic acid molecules by a weak linkage between the two sulphur atoms in the double molecule, rather than as a very stable single molecule containing two amino and two carboxyl groups.

Eleven of the twelve amino acids mentioned contain at least one asymetric carbon atom (glycocoll contains none) and are hence optically active; the levo form predominating when natural products are broken down, but not always so. It follows that each of the eleven must have at least three stereo isomers, the levo, the dextro, and inactive forms and this multiplies the number of these acids bodies by three and some of these have more than one asymetric carbon atom, this still further adding to the number of these isomeric molecules. As to the "why" of this preference for nature to deal in asymetric carbon atoms there is much darkness.

From the standpoint of the tanners craft a large percentage of the keratinous material of the hide is lost in beam-house operations, and up to the present unavoidably. This loss occurs primarily in the limes and unhairing operation. It does not follow

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that any of the twelve cleavage products enumerated may be found in this beam-house waste. These amino acids represent, in a sense, the end degradation products of the keratins, while the beam-house wastes are probably transitional protein complexes whose end cleavage products are these amino acids. It likewise appears as a result of extended study that the keratins do not readily, if at all, give a gelatin on degradation, and this seems to apply to tannery conditions as well. It is difficult accurately to guage what part a greater conservation of these epithelial structures, if it were possible, would play in the production of leather. If some of our adsorption ideas of leather-making are correct, it would seem that a successful commercial study of how to conserve the pavement epithelium of hide would add greatly to the economic wealth of the leather industry.

In microscopically examining a section of a hide we find below the epidermis a rather thick layer of what is called the true skin, derma, corium, or cutis vera, and each of these five terms means the same thing. The uppermost layer of the derma, namely the papillary layer, is made up largely as seen with the microscope of somewhat lengthened rounded eminences, which are endowed with an abundant supply of blood vessels, nerves, etc. In the finished leather this layer usually constitutes the "grain," assuming that this grain has not been modified by pressing, rolling or painting. Below the papillary layer is the reticular layer which is made up mainly of strong interlacing fibrous bands. These bands are mainly constituted of white elastic tissue and to a lesser extent of yellow. It is this fibrous layer which goes to make the major portion of leather.

It is not possible to consider the ultimate degradation products of the derma as a whole. On the contrary the various components of the cutis vera have to be examined in sequence as to the cleavage products, and like the case of the epidermis we again find that these end products are in the main amino acids. All of the twelve acids already mentioned occur frequently as cleavage molecules of other bodies than the keratins and they also occur as end products of the degradation of the derma.

In a preceding paragraph it has been mentioned that a large part of the derma is composed of white fibrous elastic tissue and an early degradation product of this tissue is collagen. The best

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definition for collagen, after having defined keratin as best we may, is that collagen is simply keratin with much less sulphur. Collagen gives the xanthoproteic and Millon reactions and also responds to the biuret test, a purplish blue coloration with copper sulphate and potassium hydroxide. Collagen's solubilities are about the same as those of the keratins and on hydrolysis (?) collagen yields gelatin as one cleavage product, thus differing from keratin.

If gelatin be split up further until definitely determinable chemical units are separable, we find again among these units numerous amino acids. Nine of the twelve amino acids mentioned as decomposition products of the keratins occur also as cleavage products of the collagens. Cystine, serine and tyrosine are absent or at least have not been separated and identified as collagen degradation products. If it be recalled that cystine occurs in largest amount among the keratin cleavage products, its absence from the collagen cleavage units is conspicuous. Glycocoll occurs in largest amount among collagen cleavage products and there are also considerable amounts of arginine and proline.

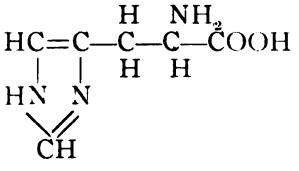
Lysine, histidine and hydroxy-proline are the additional gelatin cleavage products and a brief consideration of these three is in order.

Lysine:—α-ε-diamino-caproic acid—

$$CH_2(NH_2).(CH_2)_3.CH.NH_2.COOH.$$

A di-amino, mono-carboxylic, dextro, amphoteric acid.

Histidine:—α-amino-β-imidazolyl-propionic acid.



A mono-amino, mono-carboxylic, levo, amphoteric acid. The imino group in the heterocyclic ring probably adds to the basic character of the molecule and there is likewise a tertiary nitrogen atom.

Hydroxy-proline:—Oxy-α-pyrollidine-carboxylic acid—

$$C_5H_9NO_3.$$

A mono-amino, mono-carboxylic, levo, amphoteric acid.

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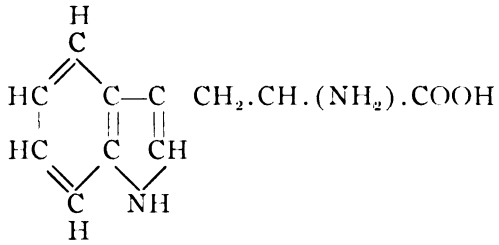
These three acids are capable of functioning only as mono-basic acids when brought into contact with a base. Each of the three has one amino group in the α position. This basic character is emphasized by another amino group in the ε position in lysine and in the case of histidine there is one imino group in the ring radical in addition to the α amino radical and there is also a tertiary N atom, in the imidiazolyl group. These three acids share the amino acids' general characteristics and these need not be repeated here.

In a preceding sentence allusion was made to an abundant supply of blood vessels in the derma of the skin. This is equivalent to stating that this structure has an abundant blood supply. A common protein body of the blood stream is serum globulin. Among the ultimate cleavage products of the globulin is the amino acid tryptophane.

Tryptophane:—β-indolyl-α-amino-propionic acid.



A mono-amino, mono-carboxylic, levo, amphoteric acid.

Tryptophane is particularly interesting because it is yielded by the degradation of many protein complexes, although not derived from gelatin. Another item of interest is the fact that tryptophane on further cleavage yields several well defined bodies such as skatole, skatolyl acetic acid, skatolyl carboxylic acid and indole.

Mention must be made of another amino acid while considering the degradation proteins of the blood supply of a hide and that acid is isoleucine derived from blood fibrin. This body has not been made from many proteins but there is little doubt that it can thus be made.

Isoleucine:—α-amino-β-methyl-β-ethyl-propionic acid—

$$CH_3.C_2H_5.CH.CH.NH_2.COOH.$$

A mono-amino, mono-carboxylic, dextro, amphoteric acid.

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Skin has not only an abundant blood supply but also a large number of smaller nerve fibers. The amino acid norleucine may be prepared directly from nerve tissue.

Norleucine:—α-amino-caproic acid—

$$CH_3.(CH_2)_3.CH.NH_2.COOH.$$

A mono-amino, mono-carboxylic, dextro-levo, amphoteric acid.

In concluding a consideration of the degradation products of hides, a passing reference must be made to ammonia, the common ultimate result of every protein fission. In a sense the eighteen acids listed above may be considered substitution products of this base. Few conclusions as to how hide is built up can be drawn from this common production of ammonia. The strength of the union between the hydrogen and nitrogen of ammonia and its substitution products, in this case amino acids, is evident. Moreover, it seems that some direct union between these two elements must exist in all protein complexes.

From what has been said it follows that we can trace each one of these eighteen amino acids back to the various proteins of the hide. It does not follow that these amino acids have been made actually from hide, for if one attempted to separate a sufficiency of nerve fibrils from hide to enable a laboratory to produce norleucine (caprine) it would call for a manipulative skill bordering on the impossible. However, there is no reason for believing that there is a wide variation in the protein of a nerve trunk or of a nerve fibril.

A glance at the preceding paragraphs indicates that hide substance has been considered only in its analytic aspect. If ammonia and the amino acids are fission products of the various protein complexes, is it possible synthetically to produce a protein? No, is the answer. No keratin, or collagen, or gelatin has ever been synthesized. An approach has, nevertheless, been made and in a few brief words the line of attack which has been used is here indicated.

If it be recalled that these amino acids possess both basic and acid characteristics in the same molecule, there is no reason why two molecules of the same acid should not combine, the basic part of the one uniting with the acidic part of the other. The simplest amino acid, glycocoll, thus unites with itself and produces glycyl-

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glycine. This body is a so-called "peptide" and is the simplest known peptide. The union of the two molecules of glycocoll takes the form of an imide linkage with the liberation of water in the reaction. Glycyl-glycine is still acid and basic in character and it is thus possible to add more glycocoll to glycyl-glycine and thus produce a "tri-peptide" and a "tetra-peptide," etc. In general the almost limitless combinations of these various amino acids produce the so-called "polypeptides."

It is of interest to note that a polypeptide has been synthesized which contains fifteen glycocoll and three leucine residues, but even this polypeptide is not a protein. Many of these peptides respond to the biuret test and are precipitable with phosphotungstic acid and in some cases it is possible to shift a sweet to a bitter taste and vice versa by changing the molecular structure of the peptide. These are characteristic properties of many proteins. But a protein is a complex vastly more elaborate than a test-tube peptide and it is almost certain we are dealing with forces which do not concern chemistry alone but reach the province of physics; and up to the present are still far beyond the present domain of all science. Our stock in trade, the hide, is not one protein but a heterogeneity of proteins.

Thus far on considering the analytic and synthetic work of hide we have considered only the proteins or nitrogenous bodies. Protein material is not the only group of bodies which may and do occur in hide even though they be of major importance.

There is always the possibility in hides of the presence, due to the blood and lymph circulation, of many substances which occur in these fluids. It will have to suffice merely to mention the possibility of the presence of some pentose and hexose sugars among the carbohydrates and also the presence of that very important carbohydrate from the stand-point of animal life, glycogen. This hexose has been separated directly from skin and in considerable amount. We know not much more of the chemical constitution of glycogen than its empirical formula $C_6H_{10}O_5$. A vast amount of work has, of course, been done on the metabolism of many of these carbohydrates.

If the presence of certain carbohydrates in the skin complex is incidental, and in certain cases perhaps essential, when the fats are reached we leave the incidental realm and reach the

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essential. Every skin has fats and sometimes in large deposits immediately below the cutis vera. These fats are perhaps for a moment best considered as fats proper, as lecithin and as cholesterol.

Using the word "fat" in a restricted sense as referring to a chemical union between one molecule of glycerose and three molecules of some one monovalent fatty acid, or mixtures of fatty acids, we frequently find such fat in evidence microscopically. Should it not be found by a simple ocular inspection of a skin its ubiquitous presence can be shown either microscopically or chemically. The microscope always reveals certain fat globules in skins and fat solvents always extract the finely divided intercellular fats as well as any other fat that may be present. We thus add to our skin complex such well defined chemical molecules as glycerose and the three common fatty acids, oleic, palmitic and stearic.

If our ordinary fats are ubiquitous inter-cellular material, the lecithins are ubiquitous intra-cellular matters. Lecithin (better lecithins) is a primary cell constituent and skin is made up of cells like all other living matter, or once living.

Lecithin is chemically a definite molecular complex of two fatty acid radicals (alike or different), one choline and one glycerophosphoric acid radical. Referring the constitution of lecithin back to glycerose two of the alcoholic hydroxyls of glycerose are replaced by two fatty acid radicals in simple ester formation, and the third hydroxyl is substituted by eliminating one hydrogen of ortho-phosphoric acid, again in simple ester formation. If a second hydrogen of phosphoric acid be replaced by the quaternary-ammonium base choline, we have a lecithin. Choline is simply trimethyl-hydroxyethyl-ammonium hydroxide ($N(CH_3)_3.CH_2.CH_2OH.OH$). The formula of a lecithin would hence be as follows and this lecithin is cholyl-distearyl-glycero-phosphoric acid.

$$\begin{array}{l} CH_2 - OOC.C_{17}H_{35} \\ | \\ CH - OOC.C_{17}H_{35} \\ | \\ CH_2O-PO-OC_2H_4 \\ \quad\quad | \quad\quad | \\ \quad\quad OH \quad\quad N(CH_3)_3 \\ \quad\quad\quad\quad | \\ \quad\quad\quad\quad OH \end{array} \qquad \text{(A lecithin).}$$

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If lecithin is an ever present cell constituent so also is cholesterol. The make-up of this fatty body and its isomer, iso-cholesterol, is largely unknown. Cholesterol is a mono-atomic alcohol and has at least one double bond in its structure, thus suggesting an analogy to the terpenes. Even its empiric formula is somewhat in doubt and it is not certain whether cholesterol occurs as such in the living cell or as an ester. This body is of special interest in sheep skins, on account of the large amount which occurs in wool fat. Comparatively little is known about this very widely distributed fat either chemically or in plant and animal metabolism.

While nearing the close of this fragmentary survey attention is simply drawn by name to quite a number of well defined bodies which have been studied as end products of metabolic processes in life, in which processes the skin shares. These well defined molecules are the end cleavage products of the nucleo-proteins always present in cell contents, particularly in the nuclei. These nucleo-proteins on cleavage go by successive steps to protein, nuclein, nucleic acid, purine and pyrimidine nucleotides, purine nucleosides, phosphoric acid, sugars, and to purine and pyrimidine bases.

Two common end purine bases of such protein cleavage are adenine (6-amino-purine) and guanine (2-amino-6-oxypurine). These two bases are readily converted into uric acid (2-6-8-trioxypurine).

Three common end pyrimidine bases of such protein cleavage are uracil (2-6-dioxypyrimidine), thymine (5-methyl-2-6-dioxypyrimidine) and cytosine (6-amino-2-oxypyrimidine).

It is not to be inferred that the above list of well defined chemical entities includes all such bodies which can be derived from hide, for this is not the case. The object of this tabulation is merely to indicate that a skin is an enormously complicated complex and that we include almost every known cleavage product of life when we try to list the degradation products of a skin. It is not strictly within the province of leather chemistry to call attention to a classification of cleavage bodies such as is used by the American Physiological Society and the American Society of Biological Chemists, in which somewhat less stress is put on ultimate cleavage products and more emphasis is laid on more com-

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plex aggregates, for biology deals with all the phenomena of life. Had it not been for the enormous amount of work which has been done by biological chemists in institutions of medical research, our knowledge of the cleavage products of hide would be meagre indeed.

As leather chemists we owe an enormous debt to our unintentional collaborators in the biological field, for we are wiser by far in our knowledge of our common raw material, skin, than is the rubber chemist about his latex, the textile worker about his cellulose, the petroleum operator about his crude, and so on.

In the speaker's humble opinion, future specific knowledge leading to broad principles of tanning will come about in co-ordinating biological knowledge with our chemical knowledge, and in the latter item we include the domain of physics.

COMMITTEE ON LIMEYARD CONTROL, II. THE ANALYSIS OF LIME LIQUORS.*

By W. R. Atkin and W. E. Palmer.

A considerable amount of work has been done on this subject in the last decade, and one might mention the names of Procter, Stiasny and Wood as pioneers in solving the complicated analytical problems dealing with these liquors. By far the most important of the recent work has been that of Bennett[1] who published an exceedingly comprehensive list of determinations to be made, which, together with the whole of the literature on the subject has been criticised and reviewed by D. Burton[2].

In the present paper the intention has been to amend certain of these methods and to point out errors that occur in some of them. The actual methods employed are not new in principle, but the more or less intimate relationships existing between these various estimations, which to a certain extent had previously been isolated in watertight compartments, have been brought to the fore. In order to emphasize these relations all results have been calculated into terms of N/10 reagents (acid or alkali as the case may be).

* Reprinted from *J. S. L. T. C.*, 4, 111 (1920).

[1] H. G. Bennett, *Collegium* (London), 1915, pp. 255-266, 313-322, 329-335; This Jour., 11, 98 (1916).

[2] D. Burton, *J. S. L. T. C.*, 1920, p. 32; This Jour., 15, 308 (1920).

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Before entering into a description of the analytical methods involved, a short account of the various substances likely to be present will, no doubt, be useful.

Firstly, we have calcium hydroxide, and if the limes have been strengthened by sodium sulphide, there will also be present sodium hydroxide and the sulphydrates of sodium and calcium. In addition, there are a large number of nitrogenous bodies arising from the solubilisation and subsequent decomposition of the proteins of the hide, hair and epidermis, to say nothing of proteins from adhering dung and blood. These proteins are hydrolyzed by the alkali, also by the enzymes and bacteria present and among the products of hydrolysis are peptones, amino acids, ammonia and amines. It has been shown by Effront and others that certain bacteria secrete enzymes termed amidases, which split up amino acids still further into ammonia, amines and fatty acids. These enzymes appear to be secreted freely in media where the conditions are unfavorable to rapid growth of the bacteria, and notably so in the case of comparatively strong alkaline solutions. In fact, considerable quantities of ammonia, acetic and butyric acids are produced commercially by the fermentation of the nitrogen containing residues from distilleries.

As a complete analysis of lime liquors would be obviously a stupendous undertaking, an attempt has been made to devise a scheme for works control that would be reasonably quick and as accurate as possible under the circumstances. It is, therefore, suggested that the determination of the following are ordinarily necessary for works control:

1. Total Nitrogen.
2. Ammonia and amines.
3. Sulphides.
4. Total Alkalinity.
5. Caustic Alkalinity.

To determine these, six estimations are necessary, and from them it is possible to calculate:

6. Amino acids.
7. Acid splitting up products of proteins combined with sodium or calcium hydroxides, and which are referred to subsequently as sodium and calcium salts of hydrolytic products.

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FILTRATION.—All liquors were filtered before analysis, using Green's folded filters No. 605, which gave very clear filtrates easily. Wood and Law[3] have pointed out the great importance of filtration as minute crystals of calcium carbonate are apt to pass through and these effect the titrations.

1. *Estimation of Total Nitrogen.*—The nitrogenous matter was estimated by the Kjeldahl method as described by Procter[4] but with one slight modification. 25 cc. of filtered lime liquor was pipetted into the digestion flask and 15 cc. conc. sulphuric acid added with a few pieces of porous pot to prevent bumping. The flask was heated carefully over a rose burner to evaporate off the water, 5 gms. of potassium sulphate added after the mixture had blackened, and then vigorously heated without the rose burner. After the liquid had become colorless or a faint yellow, the heating was continued gently for 1 hour more and the flask allowed to cool down. The liquid was then well diluted with water, 60 cc. of 40 per cent. caustic soda solution added, and the ammonia distilled over into an excess of standard acid. The excess of acid was titrated back, using carminic acid as indicator.

If the lime liquor is not an old one, or does not contain much sulphide, a larger quantity than 25 cc. can conveniently be taken but the result should be calculated back to 25 cc. in order to render all the results comparable.

2. *Estimation of Ammonia and Amines.*—Ammonia and volatile amines were estimated by distillation, using the method employed by Thompson and Suzuki[5] except that instead of neutralizing the lime liquor with acid and adding excess of magnesia, the suggestion made initially by Procter[6] and somewhat modified by Bennett[7] of employing a 10 per cent. solution of magnesium sulphate without previous neutralization by acid, was adopted. A little turpentine was added to the distillation flask to prevent frothing. After distilling at a temperature under 40° C. for 35 minutes, the acid used for absorbing the ammonia was rinsed into a large porcelain basin and boiled for a few minutes to drive off any sulphuretted hydrogen that might have come over. By adopt-

[3] J. T. Wood and D. J. Law, *Collegium*, 1912, p. 122; This JOUR., 7, 346 (1912).

[4] H. R. Procter, *Leather Chemists' Pocket Book*, p. 38.

[5] F. C. Thompson and K. Suzuki, *J. S. L. T. C.*, 1917, p. 140.

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ing this precaution of boiling, carminic acid may be employed as indicator in titrating back the excess of acid (sulphuric).

SULPHIDES.—The estimation of sulphides was carried out in the usual way, *i. e.*, by titrating 25 cc. of the lime liquor with N/10 ammoniacal zinc sulphate solution made up according to Bennett's[8] description, and using sodium nitro-prusside as external indicator. It is necessary to point out at this stage that 1 cc. of the zinc sulphate solution (containing 14.35 grm. $ZnSO_4$, $7H_2O$ per litre) corresponds to .0028 grm. of NaSH, whereas 1 cc. of N/10 HCl corresponds to .0056 grm. NaSH, so that in order to transform into cc. of N/10 acid or alkali, for comparison, the number of cc. of N/10 zinc sulphate solution used must be divided by two.

ALKALINITY.—As Bennett has pointed out, there are several factors contributing to the alkalinity of lime liquors, namely:

(*a*) Calcium hydroxide.
(*b*) Sodium hydroxide.
(*c*) Sulphydrates of calcium and sodium.
(*d*) Ammonia and amines.
(*e*) Sodium and calcium salts of weak acids, or hydrolysis products of hide proteins.

For convenience, we propose to designate these factors by the letters (*a*), (*b*), (*c*), (*d*) and (*e*) respectively.

TOTAL ALKALINITY.—This is due to all the substances enumerated above, and is determined by the method described by Bennett[9] in which 25 cc. of the filtered lime liquor is boiled with excess of N/10 sulphuric acid and the excess titrated with N/10 caustic soda, using methyl red as indicator. In all the lime liquors examined a precipitate was formed by this treatment with acid; these precipitates are due, doubtless to dissolved keratinous matter and not to true hide substance as was demonstrated by one of us recently.[10] This point was further tested by determining the total alkalinity of a solution of gelatin in lime water (dissolved in two days without heat) in which case no precipitate was obtained on addition of acid. A similar result was noted with a

[6] Procter, *L. I. L. B.*, p. 63.
[7] Bennett, *Collegium* (London), 1915, p. 262; This JOUR., 11, 98 (1916).
[8] Bennett, *Collegium* (London), 1915, p. 314; This JOUR., 11, 98 (1916).
[9] Bennett, *Collegium* (London), 1915, p. 260; This JOUR., 11, 98 (1916).
[10] Thompson and Atkin, *J. S. L. T. C.*, 1920, p. 15; This JOUR., 15, 245 (1920).

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solution of hide powder in lime water, although both solutions were very rich in nitrogen. By using N/10 reagents throughout, the titration for total alkalinity is a measure of

$$a + b + c + d + e.$$

CAUSTIC ALKALINITY.—The caustic alkalinity is an important figure for the tanner as it is a measure of the plumping power of the lime and has a pronounced influence on the subsequent leather product. This caustic alkalinity is due to the hydroxides of calcium and sodium, or to $a + b$.

Bennett[11] has devised a method to determine this figure which is very ingenious, but in one important respect unsound. One of the objects of the present paper is to correct this error so that true results may be obtained. Bennett's method depends on two titrations of the lime liquor after treatment with formaldehyde.

First Titration.—10 cc. of 40 per cent. formaldehyde solution diluted with 10 cc. of distilled water is neutralized to phenolphthalein with N/10 caustic soda until a faint pink color appears. 25 cc. of the clear filtered lime liquor is added, and, after mixing, titrated with N/10 hydrochloric acid until the pink color just disappears.

The following reactions occur:

1. The hydroxides of calcium and sodium are neutralized by the acid and not affected by the formaldehyde.

Ammonia reacts with the formaldehyde to form neutral hexamethylene tetramine.

$$4NH_3 + 6H.CHO = (CH_2)_6N_4 + 6H_2O.$$

Formaldehyde reacts with sulphydrates and liberates an equivalent amount of hydroxide—

$$NaSH + HCHO + H_2O = H.CH(OH)\ (SH) + NaOH.$$

and thus all sulphydrates are estimated.

Formaldehyde also reacts with amino acids producing methylene amino acids which react acid to phenolphthalein.

$$NH_2.R.COOH + H.CHO = CH_2 : N.R.COOH + H_2O.$$

Consequently after adding formaldehyde to a lime liquor, methylene amino acids are formed which neutralize a certain

[11] Bennett, *Collegium* (London), 1915, p. 321.

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amount of the caustic alkalies so that the caustic alkalinity and that due to sulphydrates are reduced by this acidity produced by the amino acids. In other words, this titration affords a measure of $a + b + c$ — *amino acids.*

The above explanation is that put forward by Bennett and is quite sound. It might be added that the calcium and sodium salts of the splitting up products are not affected in this titration.

Second Titration.—25 cc. of filtered lime liquor is neutralized to phenolphthalein with glacial acetic acid until the pink color is discharged, and N/10 iodine added until an unabsorbed excess is observed. N/10 caustic soda is then added until a pink color appears and finally 10 cc. of neutral formaldehyde. After mixing, the solution is titrated with N/10 caustic soda until the pink color reappears. Later, we modified this titration (originally described by Stiasny[12] by using hydrochloric acid instead of acetic acid, as the end point was found to be sharper.

Bennett states that this second titration is a measure of the acidity produced by the amino acids, the caustic alkalies having been neutralized by the acid and the sulphydrates decomposed by the iodine; consequently the number of cc. of N/10 caustic soda found in the second titration added to the number of cc. of N/10 hydrochloric acid for the first titration gives a measure of $a + b + c$.

Unfortunately he has ignored the fact that the free ammonia often present in considerable quantities, has been neutralized with the formation of ammonium acetate (or ammonium chloride), which reacts with formaldehyde to liberate an amount of acid equivalent to the amount of ammonia present in the lime liquor and also to form hexamethylene tetramine.

$$4CH_3COO\ NH_4 + 6HCHO = (CH_2)_6N_4 + 6H_2O + 4CH_3COOH$$

or, with hydrochloric acid,

$$4NH_4Cl + 6HCHO = (CH_2)_6N_4 + 6H_2O + 4HCl.$$

This omission is curious, as Bennett[13] himself advocated the use of formaldehyde to replace the distillation with caustic soda in the Kjedahl method of estimating nitrogen.

[12] Stiasny, *Collegium*, 1908, p. 373; This Jour., 3, 63 (1908).

[13] Bennett, *J. S. C. I.*, 1909, p. 292; This Jour., 4, 140 (1909).

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It will, perhaps have been noticed that no mention has yet been made of the action of amines on formaldehyde. Primary amines such as methylamine seem to react with formaldehyde in a somewhat analogous way to the reaction with amino acids as far as the NH_2 is concerned—

$$2CH_3NH_2 + 2HCHO = (CH_3N : CH_2)_2 + 2H_2O.$$

With their hydrochlorides a liberation of hydrochloric acid is obtained exactly analogous to the case of ammonium chloride. This point was tested experimentally with methylamine hydrochloride.

The secondary and tertiary amine hydrochlorides apparently do not behave in the same way as those of the primary amines. However, Effront[14] has tested for trimethylamine in many different putrefactions, but has not succeeded in detecting it, and states that only materials containing betaine (trimethylglycine) give rise to trimethylamine.

The amino acids known to be components of hide proteins do not suggest from their constitutions the likely formation of trimethylamine by putrefaction. Accordingly there will only be a relatively small error introduced by assuming that the amount of ammonia and amines obtained by distillation reacts with formaldehyde, causing the liberation of an equivalent amount of hydrochloric acid. Thus the second formaldehyde or Stiasny titration measures the amino acids plus ammonia and amines, or d + *amino acids*. The sum, therefore, of the two formaldehyde titrations is a measure of $a + b + c + d$, and by subtracting $c + d$, that is cc. of N/10 acid required for ammonia, amines and for hydrosulphides, $a + b$ is obtained, which is the caustic alkalinity of the lime liquor.

EXPERIMENTAL.—The determinations described above were performed on lime liquors widely different in character.

I. Liquor from a light leather works that had been kept in a stoppered bottle for a year.
II. A comparatively fresh liquor not saturated with lime.
III. Fresh liquor containing no sulphide.
IV. Liquor from a local tannery containing much sulphide and used for quick unhairing.

[14] Effront, *Biochemical Catalysts in Life and Industry* (Wiley), p. 665.

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V. Liquor also from a local tannery with a moderate amount of sulphide.

VI. Liquor made up in the laboratory, and containing an extremely large amount of ammonia, much more than would ever occur in practice.

In Table I experimental results are given for each of the six liquors described. These are all in terms of cc. of N/10 HCl or N/10 NaOH per 25 cc. of filtered lime liquor, and are the means of two or more determinations.

TABLE I.

	I.	II.	III.	IV.	V.	VI.
A.—Total nitrogen by Kjeldahl						
cc. N/10 HCl.....	12.1	18.0	5.2	51.7	13.6	31.6
Mgms. nitrogen	17.0	25.2	7.3	72.4	19.0	44.2
B.—Ammonia and amines (d)....	7.2	0.8	0.2	3.1	1.1	21.1
C.—Hydrosulphides (c)						
2 cc. N/10 $ZnSO_4$, $7H_2O$....	0.6	0.0	0.0	7.5	3.8	2.3
D.—Total alkalinity						
($a + b + c + d + e$).....	29.6	15.7	11.9	37.1	20.5	37.4
E.—1st Formaldehyde titration						
($a + b + c$ — *amino acids*)	12.0	7.7	10.4	19.6	16.8	11.0
F.—2nd Formaldehyde titration						
(d + *amino acids*).....	8.6	2.9	0.9	6.2	1.6	22.2

Several interesting figures may be calculated from the experimental values shown in Table I. The caustic alkalinity ($a + b$) is calculated by subtracting the values for ammonia and amines (d) and hydrosulphides (c) from the sum of the two formaldehyde titrations ($a + b + c$ — *amino acids* + d + *amino acids* = $a + b + c + d$). The sodium and calcium salts of splitting up products (e) are calculated by deducting the sum of the formaldehyde titrations ($a + b + c + d$) from the total alkalinity ($a + b + c + d + e$).

The degree of hydrolysis of the lime liquor can be calculated by the method described by Stiasny.[15]

$$a = \frac{\text{Mgms. Nitrogen by Kjeldahl}}{\text{cc. N/5 NaOH used in 2nd formaldehyde titration.}}$$

For unhydrolyzed gelatine the factor is 178, ammonia, and monoamino acids 2.8, arginine 11.2, lysin 5.6, and by calculating from

[15] Stiasny, *Collegium*, 1910, p. 181; This Jour., 5, 345 (1910).

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Van Slyke's[16] figures for analysis of completely hydrolized gelatine, the value of a is approximately 4.0; practically the same value is obtained for hydrolyzed keratin.

The percentage of hydrolysis is, therefore:

$$100\,\frac{(178 - a)}{(178 - 4)} = 0.575\,(178 - a).$$

In addition, the proportions of ammonia and amines to total nitrogen, and of the calcium and sodium salts of the splitting up products to total nitrogen have been expressed in percentages.

The above calculations are given in Table II, where no doubt the advantages by expressing all results in terms of N/10 acid or alkali will be obvious.

TABLE II.

	I.	II.	III.	IV.	V.	VI.
Caustic Alkalinity $(a+b)$ from $(E+F)-(B+C)$..	12.8	9.8	11.1	15.2	13.5	9.8
Sodium and Calcium Salts of splitting up products (e) from $D-(E-F)$.....	9.0	5.1	0.6	11.3	2.1	4.2
Percentage Hydrolysis from $a = A \div \frac{1}{2}F$.....	100%	92.4%	.93%	89%	88.6%	100%
$\% = .575\,(178 - a)$						
Percentage of Ammonia and Amines on total Nitrogen..	59.5%	4.4%	3.8%	5.8%	8.1%	66.5%
Percentage of Calcium and Sodium Salts of splitting up products on total Nitrogen..	74.4%	28.4%	11.5%	21.8%	15.4%	13.3%

In Table I it will be noted that lime liquor VI, contains much ammonia and that unlike any of the other liquors examined, the second formaldehyde titration is greater than the first. Liquor VI, was made up in the laboratory, and furnishes experimental proof of the unsoundness of Bennett's method for determining the caustic alkalinity.

A saturated solution of lime water at 15° C. contains 1.320 gms. CaO per litre, or 25 cc. consume, 11.8 cc. of N/10 HCl. Liquors I, and II, contain no sulphide, so they would appear to be unsaturated with regard to lime. The liquors containing sulphide all show a caustic alkalinity greater than that of saturated lime water as would naturally be expected.

[16] van Slyke, *Constitution of the Proteins*, by R. H. A. Plimmer, p. 80.

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Some years ago, Bennett[17] proposed as a measure of the amount of dissolved nitrogenous matter and of the age of lime liquors the difference between titrations with standard acid using phenol phthalein and methyl orange. This method had been previously described by Stiasny,[18] but has been criticized on several occasions, and is no use in the presence of sulphides. The quantity called *e* (the sodium and calcium salts of the acid splitting up products) fulfils the same purpose as the above-mentioned difference titration between methyl orange and phenol phthalein. The older the lime liquor the greater are the amounts of ammonia and of *e* formed in relation to the total nitrogen. This point is borne out in a striking manner by lime liquor I, in Table II. Its degree of hydrolysis is 100 per cent., as calculated by Stiasny's method, though this is not surprising when it is considered that it had been kept for a year. Undoubtedly, analysis of lime liquors should be made as quickly as possible, and lime liquor I, shows distinctly that decomposition goes much beyond the stage of amino acids.

ABSTRACTS.

Uses for Waste Ends of Leather Belting. By F. R. PARSONS, *Lea. World,* Aug. 12, 1920, 833. The manner of profitably disposing of quantities of leather belting waste is described. The waste consisted of short lengths from 1 to 3 inches, faulty pieces that had been cut out, longer lengths and old belts that had been discarded for various reasons. The smaller pieces were punched up into water tap washers and dressed, larger pieces were cut up into circular valve clacks and suckers suitable for the various types of pumps and oil dressed. Quantities were used for case hardening mild steel articles and finally pieces not below 3 inches in length were sold to be used in making leather door mats.

Some Methods of Utilizing Splits. *Lea. World,* Aug. 12, 1920, 830. Splits taken off in the green state can be tanned either by a vegetable or chrome process. Taken off in the crust state, whether chrome or vegetable, it is advisable to finish off in the same tannage. Heavy vegetable tanned splits can be finished up for cheap bottom stuff or for "waxed" leather. Lighter vegetable tanned splits can be glazed for use as a lining leather. Chrome tanned splits may be finished in colors, printed or embossed in imitation of box and willow leathers, or they may be finished up for suede.

[17] Bennett, *J. S. C. I.*, 1909, p. 292; *Collegium,* 1909, 194; This JOUR., 4, 143 (1909).

[18] Stiasny, *Der Gerber,* 1906, translated *J. S. L. T. C.*, 1919, p. 129.

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Chrome splits are sometimes finished up in natural color as leather for cheap football boots, etc. Heavy splits of chrome leather may be rolled for insoles, etc.

The Commercial Examination of Sulphonated Oils. By G. F. PICKERING, *J. S. C. I.*, 39, 305T (1920). Boiling sulphonated fatty acids with aqueous hydrochloric acid does not completely decompose them. The acid always causes polymerization which unfits the resultant fat for examination. Among other difficulties, the estimation of water is complicated by the charring of samples with oils of high iodine value, the formation of lactones, and in oils containing ammonia, amide formation. The volumetric method for estimating fat gives results from 3 to 20 per cent. too high. Results by decomposing with acid and shaking out with ether may be too low through formation of polyacids, too high through taking up hydroxyl group and the fat extracted with ether will contain 0.75-2.75 per cent. of combined sulphuric acid. [The author does not state how the latter was determined.—Abst.] The refractive index and fat content are proportional. The Lewkowitsch method for neutral fat gives a neutral fat with 9-13 per cent. free fatty acids. The author's method is as follows: Moisture—distillation with xylol; total fat—boiling with dilute hydrochloric acid (1:1) for low iodine value oil, for high iodine value oils—5 grams dissolved in 50 cc. pyridine, 25 cc. strong hydrochloric acid added and heated on water bath 1½ hours; when cool the liquid is extracted twice with ether; total sulphuric acid—by ashing with sodium carbonate; free sulphuric acid—by extracting with saturated brine and titrating with methyl orange; alkali salts—the brine extracts of the preceding operation are precipitated with barium chloride; alkalies—by titrating the sample dissolved in water with acid using methyl orange and calculating to sodium oxide; ammonia—by distilling into standard acid; unsulphonated oil—by dissolving in cold water, neutralizing to methyl orange with N/2 acid and extracting with ether. The ether is washed with water, with N/1 aqueous potash and finally water, after evaporating the ethereal solution the neutral fat is obtained. The soap solution is acidified and the fatty acids extracted with ether.

Chemical Control of Iron Tanning. By G. GRASSER, *Collegium*, 1920, 166. The use of iron salts for tanning has increased to such an extent that manufacturers have begun to prepare iron tanning extracts on a commercial scale. The leather chemist is now called upon to establish methods for controlling the iron liquors as well as for analyzing the extracts and leather. It is important to regulate both the concentration of ferrous and ferric iron in the liquors during tanning. Iron tannages may be readily detected by moistening a cutting with a solution of acetic acid and tannin, which changes the color from a brownish red to a bluish black. The leather may be analyzed by methods commonly used for chrome leather, the important determinations being water, ash, ferric oxide, cal-

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cium oxide, total acid, sulphuric acid, fat, and hide substance. The ferric oxide content of 7 leathers examined varied from 9 to 37 parts per 100 of hide substance. C. A.

The Utilization of Leather Waste. By A. HARVEY, *Leather World*, **12**, 724 (1920). A review of patent specifications, etc., dealing with the utilization of leather waste in the manufacture of glue, fertilizers, leather boards and leather substitutes. Leather is prepared for conversion into glue by removing the tanning agents. Vegetable leathers are prepared (1) by treating with alkali and an oxidizing agent or (2) with alkali followed by digestion with pancreatic enzymes. Chrome is removed and recovered from chrome tanned leather by treating (1) with hot acid; (2) with dilute acid followed by sodium peroxide; (3) with chlorine; or (4) with hydroxy acids or their salts. Leather board is made by mixing powdered leather with a suitable binder, such as rubber. Chrome leathers cannot be used as fertilizers because they act as poisons to plant life. After digesting vegetable tanned leather with acid, the pasty residue can be used along with other materials as a fertilizer. Destructive distillation of leather yields nitrogenous products suitable as fertilizers and about 25 per cent. of carbon equal to bone char as a decolorizing agent.

C. A.

Single Bath Chrome Tanning. By E. GRILICHES, *Z. Elektrochem.*, **26**, 342-354, 1920. The experiments were performed by rotating pieces of calf skin in the requisite solution during 24 hours at the ordinary temperature. With chromium sulphate solutions of differing acidity, that component which is in excess in the solution is more readily absorbed at the commencement of tanning; in concentrated violet solutions the more basic, in more dilute solutions the more acidic component is absorbed, whilst in green solutions a more acidic substance is absorbed than in the violet solutions. From feebly basic solutions a more acidic portion is initially absorbed, whilst strongly basic solutions yield a basic component. As soon as the skin is saturated with one component it commences the more strongly to absorb the other. Apparently the skin does not in general possess the ability of absorbing both components equally; only in strongly basic solutions are the variations in acidity comparatively slight. If during the first hours the absorbed salt is more acidic than that contained in the original solution, the total salt absorbed is also more acidic than the solution and conversely. When washed, the leather appears to retain the chromium component much more firmly than the acidic portion. Tanning can be effected by either green or violet chromium solutions, but although the rate of absorption of chromium oxide and the amount of oxide absorbed are approximately the same from either solution, a much greater amount of acid is absorbed from the green solution corresponding thus to the higher degree of hydrolysis. *J. S. C. I.*

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Acidity of Ash-Free and of Commercial Gelatin Solutions. By H. E. PATTEN and T. O. KELLEMS, *J. Biol. Chem.*, 42, 363-366, 1920. The isoelectric point of ash-free gelatin lies at $p_H = 4.8$, corresponding to a hydrogen-ion concentration of 1.59×10^{-5}, and that of commercial gelatin at $p_H = 5.64$, corresponding to a hydrogen-ion concentration of 2.28×10^{-6}.

J. S. C. I.

Properties and Constitution of Glues and Gelatines. By R. H. BOGUE, *Chem. and Met. Eng.*, 23, 5, 61, 105, 154 and 197 (1920); Abst. *J. S. C. I.*, 39, 605A (1920). There is no variation in the viscosity of solutions of normal glues with time up to 90 minutes. Vigorous agitation of a glue or gelatin solution results in a lowering of the viscosity as also does prolonged heating. Dehydration produces a reversion of "soluble" gelatin to "insoluble" collagen. At temperatures well above the melting point the viscosity increases nearly as a logarithmic function of the concentration and varies inversely as the temperature. Addition of formaldehyde, chloral hydrate, and alums increases the viscosity. Alums have no effect upon the gel strength, but the other substances decrease the strength. Nearly all electrolytes produce a lowering in gel strength, but their effect upon viscosity may be continually to increase, continually to decrease, or first to increase and later to decrease the viscosity. It is probable that the colloid aggregates of protein molecules are united into a "streptococcic thread" which would account more adequately than the older theories for the various properties of gelatin. If the gel strength remains constant the viscosity varies as the melting point, and if the normal viscosity remains constant the gel strength varies as the melting point. There appears to be no relation between the proximate constitution of glues and their gel strength and viscosities except that the water content of the air-dry glue is proportional to the gel strength. The water-retaining capacity of glues and gelatins is therefore controlled by the same factors as determine the gel strength. This varies directly as the protein nitrogen content and indirectly as the proteose and peptone nitrogen in all glues and gelatins. The amino-acid nitrogen is greater in bone glue than in hide glues, and tends slightly to increase with decrease in gel strength. The melting point and therefore the viscosity of a glue is determined normally by the balance between the protein content and that of its hydrolyzed products, but at any given uniform gel strength the melting point and viscosity will depend upon the ratio of large to small sized molecules within the protein group. As the boiling of a glue progresses it is probable that some foreign substances as chondridin, keratin, mucin, etc., become hydrolyzed and enter the solution, causing variations in the different grades. Hide and bone glues differ from each other in chemical constitution. Fish glue corresponds more closely in its composition to low-grade bone glue than to any other. Fish glue and isinglass differ from animal glues in their low content of proline, oxyproline, and tryptophane. The strength of a glue in service is a function of the gel strength and of the viscosity, and directly proportional to the melting point. The melting point method for

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evaluation of glues is recommended as yielding a true index of actual strength in service. A very full bibliography of the subject is given as follows:

MANUFACTURE, PHYSICAL PROPERTIES, AND TESTS.

Anonymous: "Water Insoluble Glues," *Sci. Am. Sup.*, 2,279 (1919), 159.

"Properties and Preparation of Glues," *Mech. Eng.*, Vol. 41 (1919), p. 382.

Technical Notes of the Forest Products Laboratory, Madison, Wis., as follows:

F2, "The Strength of Commercial Liquid Glues."
F4, "Water-Resistant Glues."
F6, "Bibliography on Casein and Casein Glues."
F7, "Some Reference to the Literature on the Manufacture and Testing of Animal Glues."
F9, "Foamy Glues."
F10, "Resistance of Animal Glue to Moist Air."
F16, "A Method of Testing the Strength of Joint Glues."

Glue, a monthly published from October, 1910, to September, 1911, East Haddam, Conn.

Alexander, J.: "The Grading and Use of Glues and Gelatines," *J. Soc. Chem. Ind.*, Vol. 25 (1906), p. 158.

Allen and Truax: "Glues Used in Airplane Parts," Natl. Advisory Committee for Aëronautics, Report 66 (1920).

Arisz, L.: "The Sol and Gel State of Gelatine Solutions," *Kolloidchem. Beihefte*, Vol. 7 (1915), p. 1.

Bancroft: "The Action of Water Vapor on Gelatine," *J. Phys. Chem.*, Vol. 16 (1912), p. 395.

Bell and Cameron: "The Flow of Liquids Through Capillary Spaces," *J. Phys. Chem.*, Vol. 10 (1906), p. 658.

Bingham: "Relation Between Viscosity and Surface Tension," *Am. Chem. J.*, Vol. 43 (1910), p. 296.

"The Viscosity and Fluidity of Matter in the Three States of Aggregation, and the Molecular Weight of Solids," *Am. Chem. J.*, Vol. 45 (1911), p. 264.

"The Variable Pressure Method for the Measurement of Viscosity," *Proc. Am. Soc. Testing Materials*, Vol. 18 (1918), p. 373.

Browne: "Water-Resistant Glues," *Chem. and Met. Eng.*, Vol. 21 (1919), p. 136.

Clark and DuBois: "Jelly Value of Gelatine and Glue," *J. Ind. Eng. Chem.*, Vol. 10 (1918), p. 707.

Coblenzl: "Setting Point of Gelatine Solutions," *J. Soc. Chem. Ind.*, Vol. 38 (1919), p. 430.

Cope, W. C.: "A Suggested Form of Viscosimeter," *J. Ind. Eng. Chem.*, Vol. 9 (1917), p. 1046.

Dawidowski: "Glue, Gelatine, etc.," 2nd ed., Philadelphia, 1905.

Digitized by Google

Dhere: "Preparation and Properties of Demineralized Gelatine," *Compt. rend.*, Vol. 150 (1910), p. 934.

Ditmar: "Bibliography of Glue," *Z. Chem. Ind. Kolloide*, Vol. 1 (1906), p. 80.

Fernbach: "Glues and Gelatines," New York, 1907.

Flowers: "Viscosity Measurement and a New Viscosimeter," *Proc. Am. Soc. Testing Materials*, Vol. 14 (1914), p. 565.

Gill: "A Study of Various Tests upon Glue," *J. Ind. Eng. Chem.*, Vol. 7 (1915), p. 102.

Hatschek: "The Shape and Orientation of Gas Bubbles in Gelatine," *Kolloid Z.*, Vol. 15 (1914), p. 226.

Hauseman: "Glue for Use on Airplanes," *J. Ind. Eng. Chem.*, Vol. 9 (1917), p. 359.

Herschel: "The MacMichael Torsional Viscosimeter," *J. Ind. Eng. Chem.*, Vol. 12 (1920), p. 282.

Hopp: "Determination of the Tensile Strength of Glue," *J. Ind. Eng. Chem.*, Vol. 12 (1920), p. 356.

Hulbert: "Improved Apparatus for Testing the Jelly Strength of Glues," *J. Ind. Eng. Chem.*, Vol. 5 (1913), p. 235.

Jones, H. C.: "The Conductivity and Viscosity of Solutions," *Am. Chem. J.*, Vol. 36 (1906), p. 325.

Kahrs: "Glue Handling" East Haddam, Conn., 1906.

Kissling: "Advances in the Chemistry and Industry of Glue," *Chem. Z.*, Vol. 35, p. 423.

Kruger: "Optical Rotation of Antipeptone from Gelatine," *Z. physiol. Chem.*, Vol. 38 (1903), p. 320.

Kuttner and Ulrich: "Glue Testing by Cambon's Fusiometer," *Z. offent. Chem.*, Vol. 13 (1907), p. 121.

Levites: "Effect of Temperature on Gelation," *Kolloid Z.*, Vol. 2 (1908), p. 240.

Lillie: "Osmotic Pressure of Gelatine," *Am. J. Physiol.*, Vol. 20 (1907), p. 127.

Linder and Frost: "Effect of Heat Treatment on Strength of Glues," *Eng. News*, Vol. 72 (1915), p. 178.

"Specifications and Tests of Glue," *Proc. Amer. Soc. Testing Materials*, Vol. 14 (1914), Part 2, p. 509.

Low, W. H.: "Testing the Strength of Glue Jellies," *J. Ind. Eng. Chem.*, Vol. 12 (1920), p. 355.

Lowenstein: "Machinery Used in Glue Manufacture," *Trans. Am. Inst. Chem. Eng.*, Vol. 10 (1917), p. 105.

Patterson and Benson: "Setting of Gelatine," *J. Home Econ.*, Vol. 2, p. 656.

Poiseuille: "Resistance to Liquid Flow," Academie des Sciences, Recueuil des Savants Etrangers (1842), Annee (1846).

Powell, J. R.: "Chemical Control of Gelatine Manufacture," *J. Ind. Eng. Chem.*, Vol. 8 (1916), p. 932.

Digitized by Google

Powell, R. W.: "Glue Statistics," Brooklyn, 1893.
"The Relation of the Pure Food Law to Gelatin," Simmons Spice Mill, Vol. 38 (1915), p. 1084.
"Some Qualities of Glue," Brooklyn, 1897.
Ranken and Taylor: "The Viscosity of Solutions," *Trans. Roy. Soc. Edinburgh,* Vol. 45 (1905-7), p. 397.
Rideal: "Glue and Glue Testing" 2nd ed., New York, 1863.
Rudeloff: "Determination of the Adhesiveness of Glue," *J. Soc. Chem. Ind.,* Vol. 37 (1919), p. 743a.
Sammet: "Determining the Comparative Melting Points of Glues as a Measure of Jelly Strength," *J. Ind. Eng. Chem.,* Vol. 10 (1918), p. 595.
Schwerin: "Electro-endosmotic Purification of Glue," *Chem. Ab.,* Vol. 11 (1917), p. 2,625.
Scott: "The Thermal Expansion of Solutions of Gelatine in Water," *J. Phys. Chem.,* Vol. 18 (1914), p. 677.
Steinholtz: "Technical Analysis of Glue," *Chem. Z.,* Vol. 36 (1913), p. 1505.
Taggart: "Glue Book; How to Select, Prepare, and Use Glue," Repub. pub.
Thiele: "The Manufacture of Gelatine," *J. Ind. Eng. Chem.,* Vol. 4 (1912), p. 446.
Trotman and Hackford: "Conditions Affecting the Foaming and Consistency of Glues," *J. Soc. Chem. Ind., Vol.* 25 (1906), p. 104.
Watson: "Glue and Glue Testing" *J. Soc. Chem. Ind.,* Vol. 23 (1904), p. 1189.
White: "Fish Isinglass and Glue," Bur. of Fisheries Doc. 852 (1917).

CHEMICAL CONSTITUTION AND STRUCTURE.

Alexander, J.: "Albuminoids or Scleroproteins," Allen's Commercial Organic Analysis, 4th ed., Philadelphia, 1913, Vol. 8, pp. 581-629.
Bogue, R. H.: "Some Colloidal, Physical and Chemical Relationships in Glues and Gelatines," *J. Soc. Chem. Ind.,* in print.
Dakin: "Racemized Proteins," *J. Biol. Chem.,* Vol. 13 (1912), p. 357; Vol. 15 (1913), p. 271.
Fischer, Emil: "Untersuchungen uber Aminosauren, Polypeptide, und Proteine," Berlin, 1906.
Galeotti: "Condensation of Amino Acids with Formaldehyde," *Biochem. Z.,* Vol. 53 (1913), p. 474.
Gamble: "On the Properties of Certain Collagenous Bodies," *J. Soc. Chem. Ind.,* Vol. 29 (1910), p. 65.
Gortner: "The Origin of Humin Formed by Acid Hydrolysis of Proteins," *J. Biol. Chem.,* Vol. 26 (1916), p. 177.
"Hydrolysis of Proteins in the Presence of Extraneous Materials, and the Origin and Nature of Humin," *Science,* Vol. 48 (1919), p. 122.
Gortner and Blish: "On the Origin of Humin," *J. Am. Chem. Soc.,* Vol. 37 (1915), p. 1630.

Digitized by Google

Gortner and Holm: "On the Origin of the Humin Formed by the Acid Hydrolysis of Proteins," *J. Am. Chem. Soc.*, Vol. 39 (1917), p. 2477; Vol. 42 (1920), pp. 632, 821.

Harding and MacLean: "A Colorimetric Method for the Estimation of Amino Acid Nitrogen," *J. Biol. Chem.*, Vol. 20 (1915), p. 217.

Hardy: "Physical Structure of the Colloids," *Am. J. Physiol.*, Vol. 24 (1899), p. 158.

Hofmeister: "Collagen," *Z. physiol. Chem.*, Vol. 2, p. 299.

Holm: "A Modification of the Apparatus for the Determination of Arginine Nitrogen by Van Slyke's Method," *J. Am. Chem. Soc.*, Vol. 42 (1920), p. 611.

Jodidi: "Abnormalities in the Formol Titration Method," *J. Am. Chem. Soc.*, Vol. 40 (1908), p. 1301.

Kober: "Improvements in the Copper Method for Estimating Amino Acids," *J. Ind. Eng. Chem.*, Vol. 9 (1917), p. 501.

Kober and Sugiura: "A Micro-chemical Method for the Determination of *a* and *b* Amino Acids and Certain Derivatives," *J. Am. Chem. Soc.*, Vol. 35 (1913), p. 1546.

Kossel: "Racemized Proteins," *Z. physiol. Chem.*, Vol. 78 (1912), p. 402.

Levene and Lopez-Suarez: "Mucins and Mucoids," *J. Biol. Chem.*, Vol. 36 (1918), p. 105.

Levine and Beatty: "Analysis of the Cleavage Products of Gelatine," *Z. physiol. Chem.*, Vol. 49 (1904), p. 252.

Lumiere and Seyewetz: "Action of Formaldehyde on Gelatine," *Bull. Soc. Chim.*, Vol. 35 (1906), p. 872.

Muller: "Precipitation of Gelatine by Tannin," *Z. angew. Chem.*, Vol. 15 (1902), p. 482.

Okuda: "Hydrolysis of Fish Gelatine," *J. Soc. Chem. Ind.*, Vol. 36 (1917), p. 513.

Plimmer: "The Chemical Constitution of the Proteins," Vols. 1 and 2, New York, 1913.

Potter and Snyder: "Amino Acid Nitrogen of Soil," *J. Am. Chem. Soc.*, Vol. 37 (1915), p. 2219; *J. Ind. Eng. Chem.*, Vol. 7 (1916), p. 1049.

Robertson: "The Physical Chemistry of the Proteins," New York, 1918.

Roxas: "The Reaction Between Amino Acids and Carbohydrates as a Probable Cause of Humin Formation," *J. Biol. Chem.*, Vol. 27 (1916), p. 71.

Schryver: "Digestion Products of the Proteins," Allen's Commercial Organic Analysis, 4th ed., Philadelphia, 1913, Vol. 8, pp. 467-495.

Skraup and Biehler: "On the Constitution of Gelatine," *Monatsh.*, Vol. 30 (1909), p. 467.

Sörensen: "Enzyme Studies. The Formol-Titration," *Biochem. Z.*, Vol. 7 (1907), p. 45; Vol. 25 (1910), p. 1.

Tolman and Stearn: "The Molecular Mechanism of Colloidal Behavior," *J. Am. Chem. Soc.*, Vol. 40 (1918), p. 264.

Trotman and Hackford: "The Differentiation of the Different Forms of Nitrogen in Glue," *J. Soc. Chem. Ind.*, Vol. 23 (1904), p. 1072.

Digitized by Google

Van Slyke, D. D.: "The Analysis of Proteins by Determination of the Chemical Groups Characteristic of the Different Amino Acids," *J. Biol. Chem.*, Vol. 10 (1911-12), p. 15; Vol. 22 (1915), p. 281; Vol. 23 (1915), p. 411.

"The Quantitative Determination of Aliphatic Amino Groups," *J. Biol. Chem.*, Vol. 9 (1911), p. 185; Vol. 12 (1912), p. 275; Vol. 16 (1913-14), p. 121; Vol. 23 (1915), p. 407.

Van Slyke and Hiller: "Direct Determination of Non-Amino Nitrogen in the Products of Protein Hydrolysis," *J. Biol. Chem.*, Vol. 39 (1919), p. 479.

Von Weimarn: "Grundzuge der Dispersoid Chemie," Dresden, 1911.

COLLOIDAL CONSIDERATIONS, AND SIGNIFICANCE OF HYDROGEN ION.

Alexander, J.: "Colloids," New York, 1919.

Allen: "Gelatine," *Analyst* (1897), p. 258.

Bancroft, W. D.: "The Theory of Colloid Chemistry," *J. Phys. Chem.*, Vol. 18 (1914), p. 549.

"The Theory of Emulsification," *J. Phys. Chem.* Vol. 16 (1912), pp. 177, 345, 475; Vol. 17 (1913), p. 501; Vol. 19 (1915), pp. 275, 513; Vol. 20 (1916), p. 1.

Bayliss: *Proc. Roy Soc.* (London), B, Vol. 84 (1911), p. 253.

Bechold: "Colloids in Biology and Medicine," New York, 1919.

Berczeller: "Colloids," *Kolloid Z.*, Vol. 21 (1917), p. 63.

Biltz and von Vegesack: "On the Osmotic Pressure of Colloids," *Z. phys. Chem.*, Vol. 68 (1909), p. 357; Vol. 73 (1910), p. 481.

Blasel and Matula: "Acid Combining Capacity of Normal and Deaminized Gelatine," *Biochem. Z.*, Vol. 58 (1914), p. 417.

Briggs and Schmidt: "Experiments on Emulsions," *J. Phys. Chem.*, Vol. 19 (1915), p. 479; Vol. 24 (1920), pp. 120, 147.

Briggs and Hieber: "Note on the Liquefaction of Gelatine by Salts," *J. Phys. Chem.*, Vol. 24 (1920), p. 74.

Burton: "The Physical Properties of Colloidal Solutions," London, 1916.

Clayton: "The Modern Conception of Emulsions," *J. Soc. Chem. Ind.*, Vol. 38 (1919), p. 113.

Fenn: "The Effects of Electrolytes on Gelatine, and Their Biological Significance," *J. Biol. Chem.*, Vol. 33 (1918), pp. 279, 439; Vol. 34 (1918), pp. 141, 415.

Fischer, M.: "Edema and Nephritis," 2nd ed., New York, 1915.

"On Hydration and Solution in Gelatine," *Science*, Vol. 42 (1915), p. 223.

Fischer and Hooker: "Fats and Fatty Degeneration," New York, 1917.

"On the Swelling and Solution of Protein in Polybasic Acids and Their Salts," *Science*, Vol. 46 (1917), p. 189; *J. Am. Chem. Soc.*, Vol. 40 (1918), p. 272.

Fischer and Coffman: "On the Liquefaction or 'Solution' of Gelatine in Polybasic Acids and Their Salts," *J. Am. Chem. Soc.*, Vol. 40 (1918), p. 303.

Digitized by Google

Freundlich: "Kapillarchemie," Leipsig, 1909.

On the Theory of Coagulation," *Kolloid Z.*, Vol. 23 (1918), p. 163.

Freundlich and Ishizaka: "The Rate of Coagulation of Aluminum Hydroxide Sols as Measured by the Viscosity Change," *Trans. Faraday Soc.*, Vol. 9 (1913), p. 66.

Garrett, H.: "Structure and Viscosity in Gelatine Solutions," *Phil. Mag.*, 6th Ser., Vol. 6 (1903), p. 374.

Graham and Graham: "Retardation by Sugars of Diffusion of Acids in Gels," *J. Am. Chem. Soc.*, Vol. 40 (1918), p. 1900.

Hatschek: "The General Theory of Viscosity of Two-Phase Systems," *Trans. Faraday Soc.*, Vol. 9 (1913), p. 80.

"An Introduction to the Physics and Chemistry of Colloids," Philadelphia, 1916.

Henri: "The Determination of the Size of Colloidal Particles," *Trans. Faraday Soc.*, Vol. 9 (1913), p. 47.

Katz: "The Laws of Swelling," *Kolloidchem. Beihefte*, Vol. 9 (1917), p. 1.

King: "The Degree of Dispersion of Colloids and Its Determination," *J. Soc. Chem. Ind.*, Vol. 38 (1919), p. 4.

Kober: "A New Form of Ultra-filter," *J. Am. Chem. Soc.*, Vol. 40 (1918), p. 1226.

Kuster: "Uber Zonenbildung in Kolloidalen Medien," Jena, 1913.

Lewis: "Properties of the Colloidal State, and Their Application to Industry," *J. Soc. Chem. Ind.*, Vol. 38 (1919), p. 11.

Loeb, J.: "The Mechanism of Antagonistic Salt Action," *Proc. Nat. Acad. Sci.*, Vol. 1 (1915), p. 473.

"Influence of Ions on the Electrification and Rate of Diffusion of Water Through Membranes," *Ibid.*, Vol. 5 (1919), p. 440.

"The Similarity of the Action of Salts Upon the Swelling of Animal Membranes and of Powdered Colloids," *J. Biol. Chem.*, Vol. 31 (1917), p. 343.

"Ionization of Proteins and Antagonistic Salt Action," *Ibid.*, Vol. 33 (1918), p. 531.

"The Stoichimetrical Character of the Action of Neutral Salts Upon the Swelling of Gelatine," *Ibid.*, Vol. 34 (1918), p. 77.

"The Influence of Neutral Salts Upon the Viscosity of Gelatine Solutions," *Ibid.*, Vol. 34 (1918), p. 395.

"The Influence of Neutral Salts, Bases and Acids on the Precipitability of Gelatine by Alcohol," *Ibid.*, Vol. 34 (1918), p. 489.

"The Influence of Electrolytes Upon the Osmotic Pressure of Gelatine Solutions," *Ibid.*, Vol. 35 (1918), p. 497.

"Amphoteric Colloids," *J. Gen. Physiol.*, Vol. 1 (1918-19), pp. 39, 237, 363, 483, 559.

"Influence of Electrolytes on the Electrification and Rate of Diffusion of Water Through Collodion Membranes, etc.," *J. Gen. Physiol.*, Vol. 1 (1918-19), p. 717; Vol. 2 (1919-20), pp. 87, 173, 255, 273, 387.

Long and Hull: "On the Combination of Protein with Halogen Acids," *J. Am. Chem. Soc.*, Vol. 37 (1915), p. 1593.

Digitized by Google

Mathews: "Surface Tension of Ions an Important Factor in Determining the Precepitation of Colloids by Electrolytes," *Am. J. Physiol.*, Vol. 14 (1905), p. 203.

Michaelis: "Die Wasserstoffionenkonzentration," Berlin, 1914.

Moeller: "Rhythmic Diffusion Structure in Gelatine Salt Gels," *Kolloid Z.*, Vol. 20 (1917), p. 242; Vol. 22 (1918), p. 155; Vol. 23 (1918), p. 11.

Ostwald, Wo.: "A Handbook of Colloid Chemistry," Philadelphia, 1919.

"An Introduction to Theoretical and Applied Colloid Chemistry," New York, 1917.

"The New Theory of Colloid Chemistry," *Kolloidchem. Beihefte*, Vol. 4 (1912), p. 1.

"The Importance of Viscosity for the Study of the Colloid State," *Trans. Faraday Soc.*, Vol. 9 (1913), p. 34.

Ostwald and Mundler: "On Osmosis and Swelling in Disperse Systems," *Kolloid Z.*, Vol. 24 (1919), p. 7.

Pauli: "On the Swelling and Viscosity of Gelatine," *Fortschritte naturwiss. Forschung.*, Vol. 4 (1912), p. 245.

"The Viscosity and Electrochemistry of Protein Solutions," *Trans. Faraday Soc.*, Vol. 9 (1913), p. 54.

Pauli and Hirschfeld: "Acid Combining Capacity of Normal and Deaminized Gelatine," *Biochem. Z.*, Vol. 62 (1914), p. 245.

Patten and Johnson: "Effect of Hydrogen Ion Concentration on the Liquefaction of Gelatine," *J. Biol. Chem.*, Vol. 38 (1919), p. 179.

Plimmer: "Practical Organic and Bio-Chemistry," New York, 1918.

Poschl: "The Chemistry of Colloids," London, 1910.

Powis: "The Transference of Electricity by Colloid Particles," *Trans. Faraday Soc.*, Vol. 11 (1915), p. 160.

Procter: "The Equilibrium of Dilute Hydrochloric Acid and Gelatine," *Kolloidchem. Beihefte*, Vol. 2 (1911), p. 243; *J. Chem. Soc.*, Vol. 105 (1914), p. 313; This JOUR., **9**, 207 (1914).

"On the Action of Dilute Acids and Salt Solutions on Gelatine," *J. Chem. Soc.*, Vol. 100 (1911), p. 342; This JOUR., **6**, 270 (1911).

Procter and Burton: "The Swelling of Gelatinous Tissues," *J. Soc. Chem. Ind.*, Vol. 35 (1916), p. 404; This JOUR., **11**, 275 (1916).

Procter and Wilson: "The Acid-Gelatine Equilibrium," *J. Chem. Soc.*, Vol. 109 (1916), p. 307; This JOUR., **11**, 261 (1916).

Robertson: "Studies in the Chemistry of the Ion-Proteid Compounds," *J. Biol. Chem.*, Vol. 2 (1907), p. 317.

"Studies in the Electrochemistry of the Proteins," *J. Phys. Chem.*, Vol. 15 (1911), p. 521.

Sauer: "Colloid Chemistry and the Glue Industry," *Kolloid Z.*, Vol. 17 (1915), p. 130.

Schmidt: "Changes in the H and OH Ion Concentrations Which Take Place in the Formation of Certain Protein Compounds," *J. Biol. Chem.*, Vol. 25 (1916), p. 63.

Digitized by Google

Sörensen: "Coagulation of Proteins Due to Changes in Hydrogen Ion Concentrations," *Biochem. Z.*, Vol. 31 (1911), p. 397.

Svedberg, The.: "Die Methoden zur herstellung Kolloider Lösungen," Dresden, 1909.

Taylor: "Colloids," New York.

Thomas: "A Review of the Literature of Emulsions," *J. Ind. Chem.*, Vol. 12 (1920), p. 177.

Von Schroeder: "On Gellation and Swelling Phenomena of Gelatine," *Z Phys. Chem.*, Vol. 45 (1903), p. 75.

Von Weimarn: "Grundzuge der Dispersoidchemie," Dresden, 1911.

Whitney and Ober: "Colloids," *J. Am. Chem. Soc.*, Vol. 23 (1901), p. 856.

Wilson: "Theory of Colloids," *J. Am. Chem. Soc.*, Vol. 38 (1916), p. 1982; This JOUR., **12**, 122 (1917).

Zsigmondy-Spear: "The Chemistry of Colloids," New York, 1917.

On the Swelling of Gelatine in Hydrochloric Acid and Caustic Soda. By DOROTHY JORDAN LLOYD, *The Biochemical Jour.*, April, 1920; *J. Soc. Leather Trades' Chem.*, IV, 163-186 (1920). In 1900 Hardy promulgated the view that gelatine jellies are two-phase systems, one phase being a solid solution of water in gelatine and the other a liquid solution of gelatine in water, the solid phase forming an open framework throughout the system. But Procter discarded the two-phase theory as gratuitous and put forth the theory that gelatine consists of a *molecular* network. It is the hope of the author to establish the thesis that both physical and chemical heterogeneity are essential to the gel state and to show that the volume occupied by a gelatine jelly is determined by the resultant of two opposing sets of forces localized respectively in the two phases of the jelly.

Coignet's *Gold Label* gelatine was used for all experiments. In each experiment a disc of gelatine weighing from 0.05 to 0.08 g. was put into a Gooch crucible and suspended by a thread into 150 cc. of solution contained in a wide-mouth bottle with a ground-in stopper and the bottle was kept in a thermostat at 20°. A few drops of toluol were added to prevent the development of bacteria and moulds. Three sets of time curves are given showing the extent of swelling of gelatine in various concentrations of acid and alkali. The amount of swelling is also plotted against the value of P_H for the solution; points of maxima occur between 2 and 3 on the acid side and between 11 and 12 on the alkaline side, while the point of minimum is apparently assumed to occur at 4.6.

The reaction: gelatine + HCl $\leftrightarrows$ gelatine hydrochloride was found to be reversible. On the other hand the combination with soda to form sodium gelatinate appears to be irreversible. When an acid solution of gelatine was neutralized and treated with a saturated solution of ammonium sulphate, a flocculent precipitate formed which was insoluble in cold water, but, after washing, it dissolved readily in hot water and set to a jelly upon cooling. When an alkaline solution of gelatine was similarly treated, a precipitate formed upon adding the ammonium sulphate, but it dissolved

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readily in a small volume of cold water and would not set to a jelly even after concentrating.

The molecular weight of gelatine is calculated to be about 10,000 and its equivalent weight 1/13 of that figure.

If jellies which are swelling in dilute HCl or NaOH are lifted out of the liquid into the vapor phase, they immediately contract and express fluid. Often this action is so great that in a few minutes drops of liquid can be seen gathering at points all over the surface of the jelly. The water does not merely drip away from the lowest edge of a suspended jelly, but is squeezed out at definite loci scattered evenly all over the free surface of the jelly. The author claims that this confirms the idea of the existence of definite pores in a jelly surface, which was postulated by van Bemmelen and Bütschli. This phenomenon of recoil is also a good demonstration of the existence of elastic forces within the jelly, which must be localized in the solid framework. It is greatest for jellies at the point of maximum swelling, those which have been swollen in N/200 HCl or N/200 NaOH. The expressed fluid is always nearer to the neutral point than the acid or alkaline solution in which the jelly was swollen. Jellies which have been swollen in HCl or NaOH of concentration greater than N/20 do not lose water when transferred to the vapor phase, but actually absorb more water, the more so the greater the concentration of acid or alkali from which they have been taken. In some of the stronger solutions, the jelly ultimately liquefies, the gelatine dissolving in the absorbed solution.

It seems to the author that the behavior of swollen jellies in a vapor phase can be most easily interpreted by the theory that it is determined by a solid framework in the jelly, which possesses elastic properties. The stretching force in the jelly may be taken to be the osmotic pressure of the gelatine salts in solution. The forces of recoil appear to conform to Hooke's law, *stress varies as the strain;* they become greater the more swollen the jelly. Acid or alkali of N/200 produce the greatest swelling and jellies from such solutions also show greatest recoil when lifted into the vapor phase. As the concentration increases the gelatine passes from the solid external phase to the fluid internal phase. This gradual corrosion of the solid framework is accompanied by a decrease of elastic properties until finally they vanish, the framework ceases to exist and the whole system becomes a hydrosol.

The author finally makes the following statements regarding gelatine and its properties: Gelatine is an amphoteric substance which can exist as the free base (or acid) or as a salt in combination with an acid or base. Pure neutral gelatine is stable only at the iso-electric point ($P_H + = 4.6$); it is slightly soluble in hot water, but insoluble in cold water, and has the power of combining with water. At $P_H + < 4.6$ gelatine acts as a base and combines with HCl to form soluble, ionizable salts, hydrochlorides. Gelatin is a multi-acid base and combines with increasing quantities of acid as the reaction of the solution becomes more strongly acid.

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At about $P_H = 2.5$ gelatine exists mainly in the salt form. At $P_H > 4.6$ gelatine acts as an acid and combines with NaOH to form a soluble, ionizable, so-called sodium gelatinate. Gelatine is a multi-basic acid and combines with increasing quantities of base as the reaction of the solution becomes more strongly alkaline. At $P_H = 13$ gelatine exists mainly in in the salt form. Gelatine acts more readily as an acid than as a base; its dissociation constant for H^+ is greater than for OH', and its valency towards bases is greater than towards acids. The formation of keto salts in acids and enol salts in alkalies is postulated, ordinary gelatine being taken as a keto compound. All of the foregoing figures apply to a system at 20°.

Jellies are two-phase structures which can only be formed in the first place from a fluid system: *i. e.*, by cooling, and consist of a solid framework of precipitated neutral gelatine combined with some water and of an interstitial fluid which is a solution of gelatine in the salt form. The volume of a jelly is determined by the equilibrium between two opposing sets of forces; the elastic forces of the solid framework which tends to make the volume contract and the osmotic forces of the ionized gelatine salts dissolved in the interstitial fluid which tend to make the volume expand. Neutral gelatine at the iso-electric point cannot make a stable gel, since the constituent of only one phase is present. The gel formed on cooling will be free to contract till it is solid throughout and is no longer a gel. Gelatine in the salt form cannot make a gel, since the constituent of only one phase is present; in this form it will yield only sols with water. The proportion of neutral gelatine to gelatine salts in any system is determined by the reaction of the system.

The volume occupied by a gelatine jelly swelling in a fluid medium depends on the ratio of the mass of the dissolved electrolyte to the mass of gelatine, the geometrical form of the jelly, and the hydrogen-ion concentration of the medium. Jellies which are swelling in a weakly acid (or alkaline) medium lose water on being transferred to an atmosphere of saturated vapor. The amount of water lost by the jelly is a function of the reaction of the previous external fluid. This water loss is shown to follow from the elastic properties of the jelly and to be in accordance with Donnan's membrane theory. Van Bemmelen's theory that the surface of a jelly is to be regarded as a solid membrane, perforated by pores, is confirmed by observation. J. A. W.

Note on the Swelling of Gelatine in Hydrochloric Acid and Caustic Soda. By H. R. Procter, *J. Soc. Leather Trades' Chem.*, IV, 187-9 (1920). This is a criticism of Miss Lloyd's paper (see preceding abstract). The view held by van Bemmelen and Bütschli, whose conclusions Miss Lloyd accepts, is that a gelatine jelly has a solid framework with pores or meshes of *microscopic* size, and consequently would be two-phased since the liquid in the pores would largely be beyond the range of molecular attraction of the solid. The author, on the other hand, assumes a solid, very

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possibly crystalline, framework, but of *molecular* dimensions, so that the liquid in the pores is always within the sphere of molecular attraction of the solid framework, and the jelly may therefore be regarded as single-phased, like a crystal containing water of crystallization, and the jelly-mass can thus be in equilibrium with an external solution as a second phase. Such a mass can swell under the influence of osmotic pressure, since its ions are prevented from diffusing out of it by electrochemical attractions, but in an open network of microscopic dimensions no such effect could be produced unless it were enclosed by a semi-permeable membrane, since the internal liquid would simply diffuse out of its pores into the surrounding solution. Donnan's membrane-potential theory is also inapplicable to such an open network, because it depends upon electrical attractions and repulsions of the ions at molecular distances.

The fact that liquid can be squeezed out of a jelly by mechanical pressure does not support the two-phase any more than the one-phase theory of jellies. Nor is the fact that the liquid thus squeezed out contains soluble protein any proof that gelatine chloride exists in solution, because commercial gelatines always contain soluble hydrolytic products, such as Wo. Ostwald calls β-gelatine, from which there is no known means of purification, and which must exist in a dissolved form in the interstices of the jelly mass. This fact also invalidates such calculations as Miss Lloyd has made of the molecular weight of gelatine.

If gelatine really has a molecular weight of about 10,000, and consequently a valency of 13, it is singular that all of these valencies should behave as of equal ionization, so that the whole molecule acts like a monovalent acid of about 800 molecular weight.

Miss Lloyd's observation of the solubility of gelatine in HCl so weak as N/10 is surprising, but is probably due to the high temperature at which she worked. In future the author intends working as near the freezing point as possible.

The finding that the alkaline compound of gelatine is not reversible is very important, but further experiment is desirable, since there is abundant proof in leather manufacture that the alkaline products of collagen are reversible.

As regards the theory of jelly structure, the author still holds the one-phase theory, but does not claim that the phase is liquid, but rather of the nature of a solid solution, since it does not flow. Neither does he assert that there are no pores in a jelly, since mixtures of alcohol and gelatine solution set to a clear jelly, while it is known that the jelly is insoluble in and impermeable to alcohol, and such a jelly will swell more than an aqueous one owing to the osmotic pressure of the alcohol in its pores. As to the nature of the quantity called the "elasticity" of the jelly, no definition is attempted, but it is undoubtedly a question of molecular attraction like the elasticity of solids.

In conclusion the author states that the Procter-Wilson theory does not claim to be complete on all points, but as it does offer a mathematical conception, which, given a few constants, is capable of predicting the

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actual equilibrium which is realized experimentally, it is likely to stand until another is proposed which can do this more perfectly.

J. A. W.

Determination of Bisulphites in Extracts. By A. T. HOUGH, *Le Cuir* IX, 162-3 (1920). Dissolve 5 g. of the extract in about 100 cc. warm water, add about 10 cc. saturated bromine water, mix thoroughly and add about 10 cc. of 10 per cent. HCl. Then boil to expel excess of bromine and precipitate sulphates with $BaCl_2$ in the usual manner. The weight of $BaSO_4$ includes both sulphates and sulphites. Repeat this operation, but add no bromine water; the weight of $BaSO_4$ in the second case includes only sulphates. The difference between the two weights is a measure of the sulphite content of the extract. J. A. W.

Use of Formaldehyde in Leather Manufacture. By JOSEPH JETTMAR, *Le Cuir* IX, 229-32 and 242-46 (1920). Formaldehyde solutions of about 0.3 per cent. strength were used for preserving hides as long as 20 years ago, but such hides then required the addition of sulphurous, formic, or other acid to the soaks and of sulphide to the limes. A plumper leather may be obtained by swelling the hides with acid after they have come from the stick vats and then fixing this swelling by treatment with formaldehyde. The tanning may then be completed in strong rocker liquors followed by drumming, but without the usual disadvantages. Formaldehyde may also be used to stiffen the grain of loose hides and for fixing the hair of fur skins. Tawed skins treated with formaldehyde, neutralized, washed, fat-liquored, and bleached are resistant to hot water. J. A. W.

Modern Sole Leather Tanning. By LOUIS HOUBEN, *Le Cuir* IX, 213-18 (1920). After the usual unhairing and deliming, the hides are put through a series of suspenders containing only non-astringent tan liquors, which penetrate rapidly, and then through a second series containing oak, chestnut, or mimosa. The strength of the liquors can be increased more rapidly by using quebracho to which has been added a synthetic tanning agent. When tanning has progressed to such an extent that the hides can stand the rougher treatment, they are drummed for 30 hours in an oak or chestnut liquor whose barkometer reading is gradually raised from 75 to 90. Then 2 parts of sulphonated oil per 100 of hide are added. Instead of putting the hides into layaways, they are drummed for an hour at 35° C. with a mixture of 6 liters of water, 1.5 kg. glue, 1 kg. sulphonated oil, and 250 cc. lactic acid per 100 kg. of wet leather. The hides are then piled, pressed, retanned further to add weight and clear the color, piled again, and set out. The grain is swabbed with an emulsion of sulphonated oil and the hides are then dried with all the usual precautions. Six weeks are required for this tannage, the yield is good, and the utilization of tannin almost complete. J. A. W.

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Nature of the Insolubles in Tanning Extracts. By A. T. HOUGH, *Le Cuir* IX, 408-10 and 439-41 (1920). Insoluble matter in tan liquors is objectionable because it clogs the pores, necessitating scouring, and gives the grain a bad color. It is difficult to see how it can be of much value since it cannot penetrate the hide, which acts as a semi-permeable membrane; clear liquors actually do give better results. The insolubles might be made available for tanning by peptization, but this action is very slow. The per cent. of insolubles in extracts can be kept at a low figure by a more careful peeling of barks, by extracting in open vats rather than in autoclaves under pressure, by a suitable decantation of the extracts, and by certain clarification methods. Extraction in a vacuum gives excellent results. Extracts, like quebracho, are rendered completely soluble in cold water by the addition of certain synthetic tanning agents (about 20 per cent.) and heating to 50° C. Not all synthetic materials are suitable. It may be advisable in some cases to neutralize the free mineral acid before making the addition. Such mixtures penetrate and tan more rapidly, give a better yield, produce a clearer and finer grain, and make bleaching unnecessary. J. A. W.

Determination of the Permeability to Water of Sole Leather. By E. JALADE, *Le Cuir* IX, 372-77 (1920). The permeability of sole leather is influenced by a number of factors and the effect of the degree of tannage of the leather has already been discussed (This JOUR., 15, 537-42). It is important to recognize that the degree of tannage is usually greatest in the grain layer and least in the region between grain and flesh. In a sample having a degree of tannage of 73, the degree of tannage of the grain layer was found to be 80, of the flesh layer 62, and of the middle layer only 57. Contrary to the prevailing opinion, the grain is not highly resistant to penetration by water; we found leathers to have the same resistance both before and after the grain had been removed. Bleaching materially increases the permeability of leather to water; a certain make of leather was penetrated by water, under a 20 cm. column, in 50 minutes before bleaching, but in only 5 minutes after bleaching. Leathers with greater density are more resistant to penetration. A false resistance is produced by coating the grain with a drying oil and also by high water-soluble content. A leather containing 21.50 per cent. water-soluble matter required 24 hours for penetration, but when this soluble matter was washed out and the leather was again dried, water would penetrate it in 30 minutes. Low degree of tannage, excessive tannage to get high yields, washing after tanning, and bleaching all cause the leather to have poor resistance to water. Few leathers are very resistant. Out of 100 samples examined, 52 were penetrated in less than 30 minutes and only 13 required more than 4 hours. J. A. W.

Notes on the Work of Baldracco and Camilla on the Shake and Filter Method.* By R. LAUFFMANN, *Ledertechn. Rund.*, 12, 95 (1920). The

* Reprint this JOUR., 15, 201 (1920).

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author claims that the proof that such material is absorbed by hide powder with the filter method that should really be estimated as non-tans, has still to be produced. The reagents used by Baldracco and Camillo for the detection of non-tans are not suitable, since these give similar reactions with tannin. Therefore with the same justice it can be claimed that with the shake method all of the tannin is not absorbed by the hide powder. The procedure for the improved shake method is consistent in all essential points with a method worked out by Th. Veit (*Collegium*, 1908, 216 and 235) a long while ago, when the results obtained by this method were given in comparison with results obtained by the shake method.

G. W. S.

The Rational Manufacture of Chamois Leather. By G. A. H., *Ledertech. Rund.*, 12, 101 (1920). The manufacture of chamois leather is briefly described. After soaking the skins are unhaired with a lime paste painted on the flesh that may or may not be sharpened with sulphide. After unhairing they are then placed in a lime liquor after which they are fleshed, slicked and the grain is removed, washed in a drum with running water and bated with oropon. They are then pressed or passed through a wringer, fulled, oiled and fulled again, struck out and sorted into heavy and light skins. The skins are then dried in the open air, fulled and dried again, placed on the stuffing table and sprayed with oil when they are fulled again and dried for the last time. They are then allowed to heat and finally hung in oil for 10 days, soaked in water, struck out and degreased with calcined soda solution in a drum, pressed or wrung and washed again if necessary. After drying they are staked and finally fluffed on both sides.

G. W. S.

PATENTS.

Tanning Material and Process of Producing the Same. U. S. Patent 1,344,952. ARTHUR KOETZLE, New York, N. Y., assignor to Rohm & Haas Company. Filed June 6, 1919. A material for tanning purposes, comprising a condensation product of a chlorinated napthalenesulfonic acid with formaldehyde which product is amorphous, soluble in water and adapted to produce a light colored and strong leather.

Staining of Leather or Skins. U. S. Patent 1,345,234. MARIANO POTO, Paris, France. Filed March 25, 1916. Process for staining leather or skins which process consists in first impregnating the material with a dyeing liquor, which gives an insoluble ground, then glazing the material and finally applying to it a topping which imparts a luster to the material.

Method of Making Glazed Kid-Leather. U. S. Patent 1,345,429. MICHAEL A. ZDANOWSKI, Philadelphia, Pa. Filed April 21, 1917. In the

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preparation of a tanning solution containing salt and aluminum sulfate, the step of melting the salt and aluminum sulfate before dissolving the same in water.

Method of Seasoning Leather. U. S. Patent 1,345,430. MICHAEL A. ZDANOWSKI, Philadelphia, Pa. Filed April 21, 1917. The sub-process in the making of glazed leather, which consists in seasoning the leather with a seasoning consisting of water, nigrosin, carbolic acid, blood albumen, wood alcohol, gelatin, and formaldehyde.

Leather-Paring Machine. U. S. Patent 1,345,941. JOHANNES LOOSE, Stuttgart-Cannstatt, Germany. Filed March 27, 1916.

Method of Drying Patent-Leather. U. S. Patent 1,346,091. ERNST HINTZ, Wiesbaden, and HEINRICH SCHULZ, Worms, Germany. Filed Feb. 5, 1918. The method of drying patent leather, which consists in subjecting it to the action of ultraviolet rays all above a minimum wave length of 200 micromillimeters; substantially as described.

Process of Making Leather. U. S. Patent 1,346,385. ALLEN ROGERS, Brooklyn, N. Y. Filed May 5, 1920. In the conversion of hides and skins into leather, the process which comprises submitting the material to a mineral tanning operation and then to a treatment with shark liver oil.

Machine for Treating Hides and Skins. U. S. Patent 1,347,866. DANIEL MERCIER, Annonay, Ardèche, France. Filed Dec. 30, 1919. Serial No. 348,359.

Machine for Skiving Leather. U. S. Patent 1,348,221. CARI ALBERT HIRTH, Cannstatt, near Stuttgart, Germany. Filed Sept. 8, 1911. Serial No. 648,346.

Recovery of Proteids from Waste Liquors of the Hide-Treating Art. U. S. Patent 1,347,822. C. L. PECK, New York, N. Y., assignor to The Dorr Company, New York. Filed July 20, 1918. The method of recovering, from the waste liquors of the lime process of the hide-treating art, material available for use as a fertilizer, which consists in separating said liquors into a sludge and an effluent, precepitating the proteids contained in said effluent by subjecting them to the action of the waste liquors from the tanning process, and then heating the precipitated proteids in the presence of sodium hydroxide.

Recovery of Proteids from Waste Liquors of the Hide-Treating Art. U. S. Patent 1,347,823. C. L. PECK, New York, N. Y., assignor to The Dorr Company, New York. Substantially the same as the preceding patent using caustic lime in place of soda.

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Tanning. U. S. Patent 1,349,150. C. V. GREENWOOD, Blundellsands, near Liverpool, England. Filed July 28, 1915. A process of tanning in which the goods are first treated with a vegetable restraining colloid and subsequently treated with a tanning agent of such strength as would injure the goods except for the presence of the restraining colloid.

Process of Producing Artificial Leather and Product Thereof. U. S. Patent 1,350,281. J. LYNAH, Newburgh, N. Y., assignor to du Pont Fabrikoid Company, Wilmington, Del. Filed Oct. 23, 1915. The process which comprises embedding an open mesh woven textile fabric in a coating composition, and then combining the same with a fabric backing.

Machine for Seasoning or Finishing Leather. U. S. Patent 1,352,186. J. U. FLANAGAN, Wilmington, Del., assignor to F. F. Slocomb & Co., Incorporated, Wilmington, Del. Filed Nov. 13, 1917.

Process of Dampening Leather. U. S. Patent 1,352,244. F. J. BLATZ, Wilmington, Del., assignor to The Philadelphia Textile Machinery Company, Philadelphia, Pa. The process of treating leather to effect dampening thereof, which consists in subjecting the leather, while in a flat condition, to water in the form of fine spray in the presence of heat, whereby the body of the leather may be softened by the combined action of heat and moisture.

Process for Producing Tannate-Lime Compound Difficultly Soluble in Dilute Acids. U. S. Patent 1,352,768. RUDOLF TAMBACH, Ludwigshafen-on-the-Rhine, Germany, assignor, by mesne assignments, to The Chemical Foundation, Inc. Filed Mar. 10, 1917. The process for producing basic tannate of calcium which consists in heating a solution of calcium hydroxide, tannic acid and water for such a period as to render the product difficult in dissolving in dilute acid, filtering the product thus produced, washing the same with water and then drying and finally powdering and screening the product.

Leather Making. British Patent 143,221. C. BERNARD, Le Point du Jour, Crocq, Creuse, France. May 10, 1920. Relates to machines for removing the coarse hairs from rabbit skins, etc.

Leather Making. British Patent 144,401. J. H. FARRAR, Paragon Works, Bramley, Leeds. March 20, 1919. Machines for boarding, staking, and the like.

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CONTENTS

Elections - - - - - - - - - 649
The Mechanism of Bating: By John Arthur Wilson - - 650
Some Observations on the Determination of the True Tanning Value of Extracts According to Wilson and Kern. By G. W. Schultz and T. Blackadder - - - - - - - - 654
Rapid Estimation of Chromium in Chrome Liquor by Use of the Immersion Refractometer. By Arthur W. Thomas and Margaret W. Kelly 665
What Do We Really Determine as Vegetable Tanning Matter? By E. Schell - - - - - - - - 669
Abstracts - - - - - - - - 672

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THE MECHANISM OF BATING.*

By John Arthur Wilson.

Perhaps the most curious of all the processes involved in making leather is that of bating. Little is known of its origin because it was a secret process, but it is at least some centuries old. After the skins are taken from the lime liquors, unhaired, and washed, they are plump and rubbery, a condition not particularly suitable for putting them directly into the tan liquors. The object of bating is to prepare the unhaired skins for tanning, and originally consisted in keeping them in a warm infusion of the dung of dogs or fowls until all plumpness had disappeared and the skins had become so soft as to retain the impression of thumb and finger when pinched and sufficiently porous to permit the passage of air under slight pressure. In his book Wood[1] says:

> The object of bating or puering is to render the skins, and the resulting leather, soft and supple. * * * Puering is not only a filthy and disgusting operation, but is prejudicial to health and in the nature of it is attended by more worry and trouble than all the rest of the processes in leather making put together.

Wood made a thorough study of dungs and their action upon skins and his final opinion was that the active constituents of the dung infusions were ammonium compounds and pancreatic or similar enzymes. As a result of this work, and some practical development by others, dung has been replaced as a bating material in many tanneries by a mixture of ammonium chloride and pancreatin.

Our knowledge of the behavior of proteins in contact with aqueous solutions of acids, bases, and salts, in which the protein swells by absorption of water to an extent depending upon the nature and concentration of the electrolyte, raises the question as to whether bating is not simply a means of bringing the skins into a condition of minimum swelling, especially since such a condition would give the skins those physical properties which are widely accepted as indicative of properly bated skins. If this were so it would reduce bating to perhaps the simplest of the tannery processes.

* Reprinted from *J. I. and E. C.*, 12, 1087 (1920).

[1] "Puering, Bating and Drenching of Skins," Spon, 1912.

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Experimental.

The following experiment was made to show the comparative degrees of swelling of hide in lime water, in a bate liquor, and in water. In each of three 100 cc. graduated cylinders were placed 2 g. of "Standard" hide powder. The first was filled with saturated lime water, the second with distilled water, and the third with a bate liquor showing a value for log H^+ of —8.1. The cylinders were stoppered and shaken at intervals, and the swollen powders allowed to settle. At the end of 8 hours the volumes occupied by the powders were as follows: in lime water 41 cc., in distilled water 32 cc., and in the bate liquor 31 cc., showing that the bate liquor actually causes less swelling of hide than ordinary distilled water. A pure solution of ammonium chloride of the same concentration and alkalinity as the bate liquor produces practically the same degree of swelling.

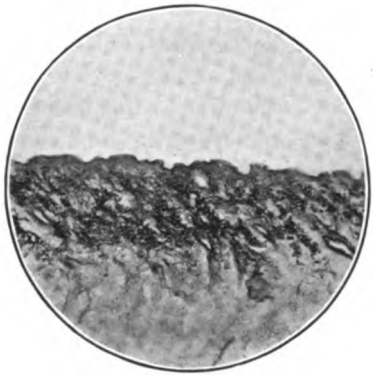

Fig. 1.—Cross section of grain and papillary layer of calf skin bated without trypsin. Note elastin fibers in upper half. Magnification 50X.

Fig. 2.—Cross section of grain and papillary layer of calf skin bated for six hours with trypsin. Elastin fibers partly removed. Magnification 50X.

A more practical test was made by comparing the action of ammonium chloride alone with that of a commercial bate, supposedly containing ammonium chloride and pancreatin. Both liquors were made up to a concentration of 1.20 g. of ammonium chloride per liter, skins of similar nature were put into each, and all other conditions kept as nearly alike as possible. At the end of several hours the skins in both liquors had all the physical properties of bated skins and no difference between the two lots could be detected, even after tanning. Recently a number of

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chemists in various parts of the country have informed the author of similar findings. This test would seem to indicate one of two things—either that pancreatin was of no practical benefit, or else that the commercial bate was deficient in enzymes.

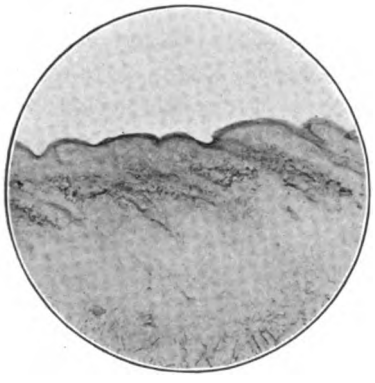

Fig. 3.—Cross section of grain and papillary layer of calf skin bated for twenty hours with trypsin. Few elastin fibers left. Magnification 50X.

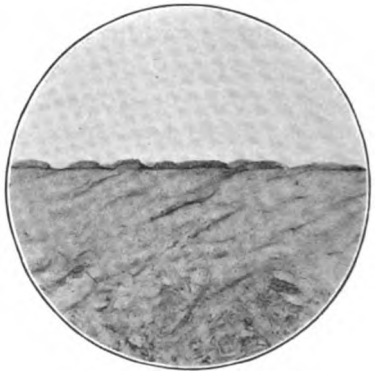

Fig. 4.—Cross section of grain and papillary layer of calf skin bated for twenty-four hours with trypsin. Elastin fibers entirely removed. Magnification 50X.

Some years ago Rosenthal[2] concluded that the bating process removes elastin from the skin. In a sample from the butt of a calfskin he found 10.36 per cent. of elastin, calculated on the dry basis, before bating, and only 0.31 per cent. after bating. But, as a measure of the elastin content of a skin, he used the per cent. of nitrogenous matter that could be rendered soluble by tryptic digestion, whereas his bating process was also supposedly a tryptic digestion. What he proved was merely that bating removed almost to completion certain nitrogenous matter from the limed skin, but whether this was elastin or hide substance which had previously been attacked by lime appears open to question.

The statement that elastin is removed by bating is also made by Moeller[3] and by Seymour-Jones,[4] who in collaboration with Wood carried out an interesting experiment on the bating of sheepskin. The "flywing" grain of a sheepskin was split from the main body of the skin, called simply flesh for convenience, and both grain and flesh were cut into halves along the backbone. One grain and one flesh were bated with pancreatin, while the other halves were

[2] This Jour., 11, 463 (1916).

[3] *Collegium*, 1918, 105, 125; *Chem. Abs.*, 12, 2706 (1918).

[4] *J. Soc. Leather Trades' Chem.*, 4, 60 (1920).

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delimed with acetic acid, but not bated. All four pieces were then tanned with sumac. There was comparatively little difference between the bated and unbated flesh halves, but the grain samples were very different from each other. The bated grain was soft and even, with the hair-holes clean and clear, but in the unbated grain the hair-holes appeared to be glued up and the surface had a rough, contracted appearance. Seymour-Jones concluded that elastin is present only in the grain membrane and that it must be digested before tanning to produce a satisfactory grain, but that bating of the skin under the grain is not only unnecessary, but often undesirable.

The results of this experiment may, however, not have been due to the bating process since one grain had been treated with acetic acid, while the other apparently had not. The author recalls having tanned in the same liquor a bated skin and one both bated and pickled. The difference between the tanned skins was striking, the pickled skin being shriveled to half of its original area and having an almost corrugated appearance, while the other had not shrunk at all and was quite smooth.

It was decided to settle definitely the question of the removal of elastin in the bating process by means of photomicrographs of cross sections of the skins taken before and after bating. The elastin fibers are not clearly discernible unless suitably stained, and for this purpose magenta has been found excellent, since it makes the elastin much darker in color, and therefore more prominent than the rest of the skin. Two liquors were prepared, each containing 1.20 g. per liter of ammonium chloride, while one also contained 0.03 g. per liter of a U. S. P. grade of trypsin. Enough alkali was added to each to make the value for log H^+ about —8.0. A piece of limed calfskin was kept in each of these liquors for 24 hours at about 37°. Microscopic examination of the sample from the trypsin liquor showed that practically all of the elastin had been removed, while, in the piece treated with ammonium chloride only, the elastin was left apparently unaltered. The test was carried out on a large scale with the same result.

The time factor in the removal of elastin can be followed by means of the photomicrographs shown in Figs. 1 to 4, inclusive.[5]

[5] Acknowledgment is made of the assistance of Mr. Guido Daub in the preparation of the photomicrographs.

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The sections, which are all 40μ thick, have been stained with magenta to make the elastin fibers more prominent. In Fig. 4 the grain membrane shows clearly enough to be measured, and is about 0.046 mm. thick. The skins are from medium-size calves, and all sections shown are taken from the butt. In a section 2.5 mm. thick the elastin fibers were present to a depth of 0.5 mm. from the grain surface, then for a distance of 1.7 mm. no elastin could be detected, but was abundant in the remaining 0.3 mm. of flesh surface. This fully confirms the view of Seymour-Jones that the main body of skin contains no elastin.

The value of removing elastin from skins must depend to some extent upon the particular properties desired in the leather, but between skins containing elastin and those from which it had been removed no such differences as were noted by Seymour-Jones could be detected, probably because the differences he found were due to causes other than bating.

Conclusion.

The mechanism of bating evidently consists of two distinct parts: (1) Reducing limed skins to a condition of minimum swelling; (2) digesting the elastin fibers present in the outer layers of the skins.

SOME OBSERVATIONS ON THE DETERMINATION OF THE TRUE TANNING VALUE OF EXTRACTS ACCORDING TO WILSON AND KERN.

By G. W. Schultz and T. Blackadder.

The official method of tannin analysis has never been considered as yielding absolute results but nevertheless has commonly been supposed to approximate very closely the actual tannin content of the tanning material when every detail of the method was rigidly adhered to. It has generally been considered that the error might be either minus or plus; that the solution is never completely detannized by hide powder and that the close approximation of the actual tannin content is obtained through a compensation of slight errors. Hence the accusations brought against the official method by Wilson and Kern[1] were startling, to say the least.

[1] This Jour., 15, 295 (1920).

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The principles involved in the method of Wilson and Kern are based on several assumptions which are neither obvious nor proven and it was in the belief that their assumptions were fundamentally wrong that this work was undertaken. The results obtained tend to show that at least two of these assumptions are erroneous and furthermore they show that we were unable to obtain concordant results as claimed for this method by the authors.

The two assumptions which appear to us particularly in error are first: The assumption that there is a definite chemical compound formed between the tannin in the tannin solution and the collagen in the hide powder during a six hours shaking, which chemical compound is stable with regard to water and also insoluble in water. And second: The assumption that one definite chemical compound is formed throughout the whole of the hide powder used in the analysis.

It appears from the results obtained by the writers that when hide powder is shaken in a tanning solution, two or three times official analytical strength, for six hours, the tannin is, to all intents and purposes completely removed from the solution. (An actual test showed that the non-tannin solution left after such shaking showed no test with gelatin salt solution until it had been evaporated under vacuum from a volume of 200 cc. to 20 cc.) When the tanned hide powder is treated with water by successive washings it appears that something is removed from the tanned hide powder which will in turn tan a second portion of hide powder sufficiently well to enable it to withstand repeated washings and still show a considerable percentage of tannin on analysis. Further, it appears to be beyond the possibility of doubt that the finer particles of the hide are tanned more completely than the coarser particles and a considerable percentage of the fine particles are more than apt to be lost during the washings. The loss of these tannin-rich particles leaves the residue proportionately tannin-poor and as the residue is what ultimately comes to analysis the final result will be too low a percentage of tannin credited to the original tanning material used.

With regard to the procedure of the Wilson and Kern method it is obvious that, the tannin being determined by difference, great care must be taken in making the four positive determinations.

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This is of especial importance in the case of the water and hide substance which are the larger ones. The importance can be visualized by considering the magnitude of the hide substance determination. This runs in most instances of tanned powder about 70 per cent., whereas the tannin figure is about 10 per cent. to 15 per cent. A half per cent. error in the hide substance determination would make a difference of 0.35 per cent. in the hide substance figure. On subtracting to get the tannin figure this error would be carried through and the tannin figure would be 0.35 out, making it 9.65 per cent. or 10.35 per cent. instead of 10.00 per cent. Thus 0.50 per cent. error has grown to a 3.50 per cent. error.

As a matter of fact, when operating with properly prepared samples of fairly constant composition we have found in general practice that check determinations will not differ by more than 0.025 per cent. in nitrogen or 0.14 per cent. in hide substance. This difference, however, is constant whether the amount of hide substance in the sample is 10 or 70 per cent. and it can be seen therefore that the percentage error in hide substance decreases with increasing amounts of the same. Thus, with a sample containing 10 per cent. hide substance the percentage error will be ± 1.4 per cent.; with a sample containing 70 per cent., ± 0.2 per cent. If we use 70 per cent. as the hide substance figure of a tanned powder and 10 per cent. as the tannin figure then the parts of tannin per 100 parts hide substance equals 14.29. Now, if we have a 0.2 per cent. error in the hide substance then we can call the hide substance figure 69.86 per cent.; the tannin figure will be increased by a corresponding amount or 10.14 per cent. and the error has been increased to 1.4 per cent.; the figure for parts of tannin per 100 parts of hide substance will be increased to 14.52 and the error to 1.6 per cent., which will be transferred to the figure for per cent. tannin in tanning material. Thus it is seen how a negligible error in the determination of hide substance is magnified eight times by the calculation involved in computing tannin by this method.

In order to eliminate as much as possible any errors that would occur in the analysis of the tanned hide powder, particular attention was given to its details. The moisture was obtained by weighing the sample into a large weighing bottle and drying at

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105-110° C. to constant weight which was usually attained in from 2 to 2½ hours. This sample was then transferred to an extraction thimble for the grease determination, in order to obviate the small error that might occur by volatilized fat that would be calculated in the moisture, and was extracted with chloroform. The nitrogen was determined in duplicate on a 1.5 g. sample in the usual manner, while a blank on the reagents and a sample of hide powder were run with each set of determinations. The hide powder serving somewhat as the opposite of the blank, namely, to give warning when the amount of ammonia distilling over was too low. Therefore we feel reasonably certain that the wide variations in the results obtained, and the great difference between them and those claimed by Wilson and Kern, must be due to causes other than errors in the analysis of the tanned powder, which would seem to invalidate this method.

In Table I is given a series of determinations on quebracho, chestnut and bisulphited quebracho. All of these determinations were run at the same time, with the exception of those given in the columns No. 4, using solutions of about twice the official analytical strength. It will be noted that the percentage error as calculated by Wilson and Kern when using the average per cent. of tannin, is surprisingly low in comparison to those reported by the latter and that there is a wide variation in the results on duplicate determinations. The washings from the two determinations on quebracho (1 and 2) were reconcentrated to 200 cc. in a vacuum pan and then used to tan a portion of hide powder which was treated in the same manner as the powders tanned with the original solutions. The resulting powder was well tanned although not as heavily as those with the original solution. The analysis which is given in column four showed that sufficient tannin was taken up from the concentrated washings and retained by the hide powder to equal 2.86 per cent. of the original tanning material used in each determination or about 5 per cent. of the average tannin value found. The results of a similar experiment with liquid chestnut extract is given in the second column 4. Here the percentage of tannin found in the wash waters equals about 20 per cent. of that found in the washed, tanned powders. It is interesting to note that for this set of experiments, using solutions of tanning material of nearly the same concentration of

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TABLE I.—Analysis of Extracts by the Wilson and Kern Method.
Strength of Liquors = Twice Analytical Strength.

	SOLID ORDINARY QUEBRACHO				LIQUID CHESTNUT				BISULPHITED QUEBRACHO		
			Shaken 6 hrs. stood 16, then shaken 2 hrs.	Washings from first 2 reconcentrated			Shaken 8 hrs. stood 16	Washings from first 2 reconcentrated			Shaken 8 hrs. stood 16
Number	1	2	3	4	1	2	3	4	1	2	3
Moisture	9.11	9.08	6.31	14.23	12.74	6.65	11.19	10.56	9.45	9.25	12.79
Grease	0.61	0.70	0.53	0.48	0.71	0.30	0.36	0.28	0.41	0.45	0.47
Ash	0.13	0.11	0.10	0.14	0.17	0.14	0.15	0.12	0.11	0.09	0.11
Hide substance	79.94	80.51	81.18	84.16	72.53	83.15	80.28	85.06	79.49	79.21	76.24
Tannin (by difference)	10.21	9.60	11.78	1.04	8.85	9.76	8.02	3.98	10.74	11.00	10.39
Tannin per 100 parts hide substance	12.77	11.92	14.51	1.23	11.41	11.73	9.99	4.68	13.51	13.88	13.63
Tanning material per 100 parts hide substance	21.49	21.49	21.49	21.49	46.55	46.55	46.55	46.55	39.39	39.39	39.39
Per cent. tannin	59.42	55.47	67.52	5.72	24.51	25.20	21.46	10.06	34.30	35.23	34.60
Average	57.45			2.86	24.86			5.03	34.77		
Per cent. tannin by O. M.	67.87				31.49				43.59		
Percentage error according to Wilson	18.1				26.7				25.3		

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tannin according to the official method and operated under the same conditions and at the same time, average values for parts of tannin per 100 parts of hide substance are obtained, that are surprisingly close in agreement. For convenient comparison these are given in Table I-A together with the actual tannin concentrations by the official method.

TABLE I-A.

	Solid Quebracho	Liquid Chestnut	Bisulphited Quebracho
Grams tannin per liter..... (According to Official Method)	8.14	8.19	9.59
Grams insolubles per liter..... (According to Official Method)	1.05	0.49	0.22
Tannin per 100 parts hide substance... (Average of duplicates)	12.35	11.57	13.70

In Table I under each of the three extracts are given the results of experiments wherein all of the conditions outlined by Wilson and Kern were adhered to with the single exception of the time in which the solution is in contact with the hide powder. After shaking for the six hours prescribed the samples stood overnight (16 hours) in their solutions and were shaken again for two hours in the morning. It will be seen that there is an increase, a decrease and practically no change, respectively, for ordinary quebracho, liquid chestnut and bisulphited quebracho, when compared with the results obtained by shaking for six hours. After considering the wide variations in results obtained by this method, of which those given in this paper are typical, it was questionable whether the results for prolonged time of contact had any significance, and we did not attempt to corroborate them. In Tables II and III are given twelve determinations with solid quebracho and liquid chestnut, respectively. In Table II the sets of determinations numbered from 5 to 10 and 11 to 16 were made at different times. In Table III the first four and last eight determinations were made at different times. It will be noted that not only do the results for the determinations made at the same time differ widely from one another but that the average of the different sets which were run at different times also differ widely. In Table III-A is given the analyses of hide powders tanned with the reconcentrated wash waters from the sets of determinations

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TABLE II.—TANNIN IN QUEBRACHO EXTRACT ACCORDING TO THE WILSON AND KERN METHOD.
Using 18 Grams per Liter.

No.	Moisture	Grease	Ash	Hide substance	Tannin (by diff.)	Tannin per 100 parts H. S.	Tannin material per 100 parts H. S.	% Tannin in extract	Average % tannin	Percentage error according to W. & K.
5	16.28	0.93	0.16	66.85	15.74	23.55	34.45	68.36		
6	16.67	0.74	0.14	67.14	15.31	22.80	34.45	66.18		
7	16.83	0.87	0.16	66.29	15.85	24.21	34.45	70.27	67.74	Nil
8	16.32	0.75	0.11	66.29	16.53	24.93	34.45	72.36		
9	16.42	0.70	0.13	67.70	15.05	22.23	34.45	64.53		
10	16.37	0.71	0.12	67.70	15.10	22.30	34.45	64.73		
11	14.76	0.70	0.08	69.66	14.80	21.25	33.93	62.63		
12	14.82	0.71	0.09	69.94	14.44	20.65	33.93	60.86		
13	14.83	0.65	0.09	70.23	14.20	20.22	33.93	59.59	64.78	40.8
14	14.60	0.60	0.13	68.26	16.41	24.04	33.93	70.85		
15	15.72	0.46	0.13	67.98	15.71	23.11	33.93	68.11		
16	15.43	0.61	0.12	69.10	14.74	21.33	33.93	62.90		

TABLE III.—TANNIN IN CHESTNUT EXTRACT ACCORDING TO THE WILSON AND KERN METHOD.
Using 36 Grams Extract per Liter.

No.	Moisture	Grease	Ash	Hide substance	Tannin (by diff.)	Tannin per 100 hide substance	Tanning material per 100 parts H. S.	% Tannin in extract	Average % tannin	Percentage error according to W. & K.
1	18.52	0.67	0.33	69.66	10.82	15.53	77.37	20.07		
2	18.72	0.63	0.33	69.83	10.49	15.02	77.37	19.41	19.68	58.9
3	18.57	0.63	0.32	69.83	10.65	15.25	77.37	19.71		
4	18.66	0.78	0.32	69.66	10.58	15.19	77.37	19.53		
5	20.72	0.82	0.12	68.15	10.19	14.95	69.16	21.62		
6	20.66	0.77	0.12	67.30	11.15	16.57	69.16	23.95		
7	20.18	0.85	0.10	67.58	11.29	16.70	69.16	24.15		
8	20.85	0.78	0.12	68.15	10.10	14.82	69.16	21.43	22.75	43.2
9	20.66	0.80	0.16	68.25	10.13	14.78	69.16	21.37		
10	20.65	0.87	0.13	67.70	10.65	15.73	69.16	22.74		
11	20.34	0.80	0.12	67.70	11.04	16.31	69.16	23.58		
12	20.71	0.93	0.13	67.42	10.81	16.03	69.16	23.18		

given in Tables II and III. All of the determinations with quebracho given in this paper were made on the same extract. The determinations with chestnut given in Table III are from the same manufacturer but those numbered from one to four are on

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a different sample from that used for the last eight determinations. Those with chestnut recorded in Table I are from a sample of different manufacture. It may be that the source or method of manufacture may have some significance in the difference in the results obtained with the washings.

TABLE III-A.—SHOWING TANNIN FOUND IN THE WASH WATER AFTER RECONCENTRATING AND APPLYING THE METHOD OF WILSON AND KERN.

	Moisture	Grease	Ash	Hide substance	Tannin (by diff.)	Tannin per 100 parts hide substance	Tanning material per 100 parts H. S.	% tannin (in six samples)	% tannin (in one sample)
Ordinary Quebracho (Solid).									
From determinations Nos. 5-10	19.42	0.65	0.96	74.16	4.81	6.49	34.45	18.83	3.14
From determinations Nos. 11-16	17.45	0.51	0.39	77.14	4.51	5.85*	33.93	24.63	4.11
Liquid Chestnut.									
From determinations Nos. 1-4	18.85	0.73	1.56	76.29	2.57	3.37	77.37	4.37	1.09
From determinations Nos. 5-12	21.69	0.74	0.14	72.08	5.35	7.42	68.77	10.80	1.35

*7/10 of the concentrated washings were used for this determination and the analysis of the hide powder is for this amount; the last two items are corrected for the whole. The remaining 3/10 were used for solids determination which was as follows: Total = 15.12; Soluble = 13.11.

It is obvious that for a given weight of hide powder, that which presents the greatest surface will combine most rapidly with tannin, and that this will be true whether the combination be strictly chemical or physical. It is well known that hide powder is a very heterogeneous material, its physical heterogeneity being partly due to its preparation and partly to the nature of the hides used. In general the smallest particles of hide will have the greatest relative surface and it is safe to assume that, per unit weight, those will fix the largest amount of tannin when in competition with larger particles, and therefore that the fine particles which pass through the cloth when washing the tanned powders will decrease the ratio of tannin per 100 parts of hide substance in the tanned powder remaining in the cloth. Furthermore the tanned powder, after it is slowly and carefully dried exhibits a great diversity in the condition of its constituent parts. It can be roughly separated into a distinctly fibrous portion of different sized fibers and a portion appearing to the naked eye as a powder

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of different sized particles. It is readily perceived that it is difficult to sample properly such a material, more so when the samples must be small as is the case with these determinations and such has been our experience. Results are given in Table IV illus-

TABLE IV.—Showing the Difference in the Ratio of Tannin to Hide Substance for Different Sized Particles.

Fine Particles Passing Through Cloth.

	Moisture	Grease	Ash	Hide substance	Tannin (by diff.)	Tannin per 100 parts hide substance	Tanning material per 100 parts H. S.	% Tannin in extract	% Tannin in extract found by W. K. method
From quebracho determinations 11 to 16	14.07	0.60	2.00	53.37	29.96	56.14	33.93	165.46	64.78
From chestnut determinations 1 to 4	16.40	0.67	0.33	49.34	33.26	67.41	77.37	87.14	19.68
From chestnut determinations 5 to 12	18.54	0.40	2.08	60.62	18.36	30.27	69.16	43.77	22.75
*Powder Tanned with Quebracho.									
Passing 100 mesh	16.72	0.75	0.14	65.45	16.94	25.88	34.45	75.12	
Passing 80 mesh	17.76	0.75	0.14	68.15	13.20	19.37	34.45	56.23	
Held by 80 mesh	16.74	0.75	0.14	67.85	14.52	21.40	34.45	62.12	
*Powder Tanned with Chestnut.									
Passing 100 mesh	17.67	0.79	0.20	63.98	17.36	25.57	77.30	33.08	
Passing 80 mesh	18.71	0.79	0.20	68.25	12.05	17.66	77.30	22.85	
Held by 80 mesh	17.97	0.79	0.20	69.38	11.66	16.81	77.30	21.74	

* The material used for these tests is a mixture of the portions remaining after analysis from several determinations. The quebracho is from the determinations five to ten. The analyses on the original hide powder with chestnut are not given in this paper; the extract used was the same as used for the results in Table IV and the results were similar.

trating and confirming these points. The fine particles were collected on a Buchner funnel. Every wash water, from the series of determinations indicated, after being squeezed through the cloth was passed through the funnel and the residue was removed from it carefully so as to prevent inclusion of fibers from the filter. Otherwise Table IV is self explanatory and shows that a

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prime fundamental on which the accuracy of the method is based is merely an assumption and is unfounded. Incidentally these results give causes for the erratic results obtained in this paper, and would seem to point to very definite reasons why accurate results could not be obtained by this method.

TABLE V.—ANALYSES OF HIDE POWDERS TANNED BY WILSON AND KERN PROCEDURE.

	Quebracho Extract 18 Grams per liter		Osage Orange Extract 30 Grams extract per liter			
Number	17	18	1	2	3	4
Procedure	Non-tans squeezed out-not washed	Same as No. 1 washed 12 times	Non-tans squeezed out, dried without washing	Same as No. 1	Same as preceding but washed 20 times	Ditto No. 3
Moisture	15.00	18.27	18.45	18.26	21.37	22.30
Grease	0.63	0.82	0.98	1.13	0.65	0.65
Ash	0.17	0.12	0.34	0.35	0.18	0.17
Hide substance	69.38	67.14	65.73	65.90	67.98	66.85
Tannin (by diff.)	14.82	13.65	14.50	14.36	9.82	10.03
Tannin per 100 parts hide substance	21.36	20.33	22.06	21.79	14.44	15.00
Tanning material per 100 parts hide substance	33.93	33.93	55.98	55.98	55.98	55.98
% Tannin	62.95	60.00	39.41	38.92	25.72	26.80
% Tanning material (T. S.) in washings	5.22	13.11	7.5	7.52	21.97	22.20
% Found by analysis of tanned powder	62.95	60.00	39.41	38.92	25.72	26.80
Total found	68.17	73.11	46.91	46.44	47.69	49.00
T. S. of extract (direct)	82.40	82.40	56.38	56.38	56.38	56.38
T. S. unaccounted for	14.23	9.29	9.47	9.94	8.69	7.38
% Loss of total solids	17.3	11.3	16.8	17.8	15.41	13.09
% Error in tannin according to Wilson and Kern		13.1			62.5	56.0

Further proof that the proposed method of Wilson and Kern is in error is exhibited in Table V. The analyses of hide powders tanned with two widely different tanning materials are given before and after washing, together with the total solids of the washings. The different determinations for each tanning material were made at the same time. With quebracho extract it will be noted that before and after washing there is a loss of 17.3 and

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11.3 per cent. of the total solids, respectively. It is evident that the sum of the per cent. tannin found in the hide powder and the per cent. total soluble solids in the washings should equal the total solids of the extract. For an increase of 7.89 per cent. in total soluble solids in the washings between the unwashed and washed sample there is only a corresponding decrease of 2.95 per cent. in tannin from the analyses of the two tanned powders. With Osage orange extract we have approximately the same percentage loss of total solids and for an average increase of 14.58 per cent. in the total soluble solids in the washings we have an average decrease of 12.91 per cent. in tannin found by analysis of the powder. When we consider the data presented in Table IV it is not surprising that such losses occur. All of the sources of error demonstrated tend toward lowering of the tannin value; the fine particles passing through the cloth when squeezing carry a greater proportion of tannin to hide substance than that remaining which is ultimately used for analysis; the fine particles in the sample prepared for analysis which contain a greater proportion of tannin to hide substance than the fibrous portion, are most difficult to incorporate in such a small sample as used for the nitrogen determination. However, the definite explanation of these losses which are beyond doubt due to this method of determining tannin, is a subject for further work. Since these losses are necessarily caused by the determination of tannin it follows that our figures for per cent. tannin are too low. It will be seen that the percentage error in tannin in these determinations are about one-third of those reported by the authors of this method for the same kind of extracts and it must be remembered that if our figures for tannin were lower then also the loss of total solids as recorded would be much greater.

The object of this paper is simply to present some typical results which summarize our observations on the proposed method of Wilson and Kern to date. We have purposely refrained from drawing hypothetical conclusions. The only conclusions made appear as definite and obvious from the data presented. The work on which this paper is based was done in the laboratories of the Elk Tanning Company, Ridgway, Pa., and of the Smethport Extract Company, Damascus, Va.

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RAPID ESTIMATION OF CHROMIUM IN CHROME LIQUOR BY USE OF THE IMMERSION REFRACTOMETER.

By Arthur W. Thomas and Margaret W. Kelly.

The immersion refractometer has proven to be a very convenient instrument in analytical chemistry. It is used for detection of watering of milk, and a rapid and very accurate analysis of mixtures of ethyl and methyl alcohols has been made possible by this instrument. Other uses, as for example, standardization of solutions, have been proposed for it but they are not so extensively applied as the methods above mentioned.

It occurred to us that the immersion refractometer could be used for quick determinations of the chrome content of chrome liquors provided a table of refractive indices corresponding to various strengths of chrome liquors was available. Such a table has been prepared and is submitted herewith. By means of it and an immersion refractometer, the chrome content of liquors can be determined in about three minutes without the use of chemicals other than water.

Chrome Liquor.—The chrome liquor used was prepared by passing sulfur dioxide into a concentrated solution of chemically pure sodium dichromate until reduction was complete, as evidenced by failure to get a test for Cr_2O_7 ion. The resulting green solution was washed free from sulfurous acid by sucking air through the liquor heated on a water bath. Any evaporation was compensated by addition of distilled water from time to time and the evidence for complete removal of sulfur dioxide was the failure of the vapor from a portion of the liquor boiled in a test-tube to bleach a strip of filter paper stained with iodine solution.

The official methods of this Association were used for analysis of the liquor. In determination of the amount of chromium it contained, a sodium thiosulfate solution that had been standardized against dried chemically pure potassium dichromate, was used.

The liquor showed upon analysis:

*Cr_2O_3 242.7 gm. per liter at 25° C.
Acid SO_3 251.7 gm. per liter at 25° C.
*Total SO_3 382.1 gm. per liter at 25° C.

Based upon the starred values, the liquor contained 52.7 g. of $Cr(OH)SO_4$ and 224.7 g. of Na_2SO_4 per liter at 25° C. This

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concentrated liquor was used for preparation of the various diluted liquors for determination of the refractometer-concentration curve, and each diluted solution was analyzed to accurately determine its chromium content.

Refractometer.—The immersion refractometer which we used was made by Carl Zeiss of Jena. All readings were made in a water thermostat at 25° ±0.005° C. The scale reading for pure water, at this temperature, was adjusted to 13.25. A description of this refractometer and method of adjustment is given in Sherman's Organic Analysis, p. 17-21; Leach's Food Inspection and Analysis, p. 97-107, and Woodman's Food Analysis, p. 11-14.

Tabulation.—The values given in Table I were read from the curve shown in Fig. 1. This "curve" of relation of refractometer readings to concentrations of chrome is a straight line. It was plotted from the averages of readings taken by each of us on two different sets of diluted liquors which were made on different days. For economy of space, these figures are not given but the points are indicated in Fig. 1.

TABLE I.—IMMERSION REFRACTOMETER READINGS OF CHROME LIQUORS.

Scale reading	Index of refraction	Grams of Cr_2O_3 per liter	Scale reading	Index of refraction	Grams of Cr_2O_3 per liter
14	1.33281	0.46	31	1.33934	13.2
15	1.33320	1.2	32	1.33972	14.0
16	1.33358	1.9	33	1.34010	14.7
17	1.33397	2.7	34	1.34048	15.5
18	1.33435	3.5	35	1.34086	16.2
19	1.33474	4.2	36	1.34124	16.9
20	1.33513	4.9	37	1.34162	17.7
21	1.33551	5.7	38	1.34199	18.4
22	1.33590	6.5	39	1.34237	19.2
23	1.33628	7.2	40	1.34275	19.9
24	1.33667	7.9	41	1.34313	20.7
25	1.33705	8.7	42	1.34350	21.4
26	1.33743	9.5	43	1.34388	22.2
27	1.33781	10.2	44	1.34426	23.0
28	1.33820	10.9	45	1.34463	23.7
29	1.33858	11.7	46	1.34500	24.4
30	1.33896	12.5	47	1.34537	25.2

This table gives the immersion refractometer readings and corresponding indices of refraction of pure chrome liquor at various dilutions.

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Sources of Error and Limitation of Method.—Since most dissolved substances raise the index of refraction of water, a commercial chrome liquor may show higher chrome content as measured by the refractometer than is actually present, due to presence of aluminum and iron salts, sodium chloride, etc. This error can be corrected, however, by comparing the chrome contents found by refractometer and hypo titration on a given shipment of concentrated liquor or crystals, and a conversion factor calculated, which when applied to the values in the table will give the true chrome content. A comparison of the values obtained by refractometer and titration will show whether or not the liquor conforms or nearly conforms to an ideal chrome liquor. The degree to which the refractometer values for Cr_2O_3 are higher than the titration values, is a measure of the amount of foreign salts in excess of $2Cr(OH)SO_4.1Na_2SO_4$.

It is inadvisable to attempt to take refractometer readings on solutions containing more than 20 gm. of Cr_2O_3 per liter because the field is too dark. It is impossible to read closer than 0.2 of a scale division on liquors containing between 20 and 35 gm. of Cr_2O_3 per liter.

The solutions must be read at 25° C. Increase or decrease in temperature results in low or high scale readings respectively. The magnitude of this temperature effect is shown in Fig. 2, where readings are shown for various temperatures of a solution which read 15.34 immersion refractometer scale at 25° C.

The refractometer scale must be checked against distilled water, and the amount to which it differs from the values set down in Table II, must be added or subtracted as the case may be, to the scale readings given by the chrome liquor. This value once obtained ought not change unless the instrument is handled roughly.

TABLE II.—IMMERSION REFRACTOMETER READINGS FOR PURE WATER.

Temp., C.	20°	21°	22°	23°	24°	25°	26°	27°	28°	29°	30°
Reading	14.5	14.25	14.0	13.75	13.5	13.25	13.0	12.7	12.4	12.1	11.8

Conclusion.—A cheap tannery control method for rapid estimation of the strengths of chrome liquors is available. This

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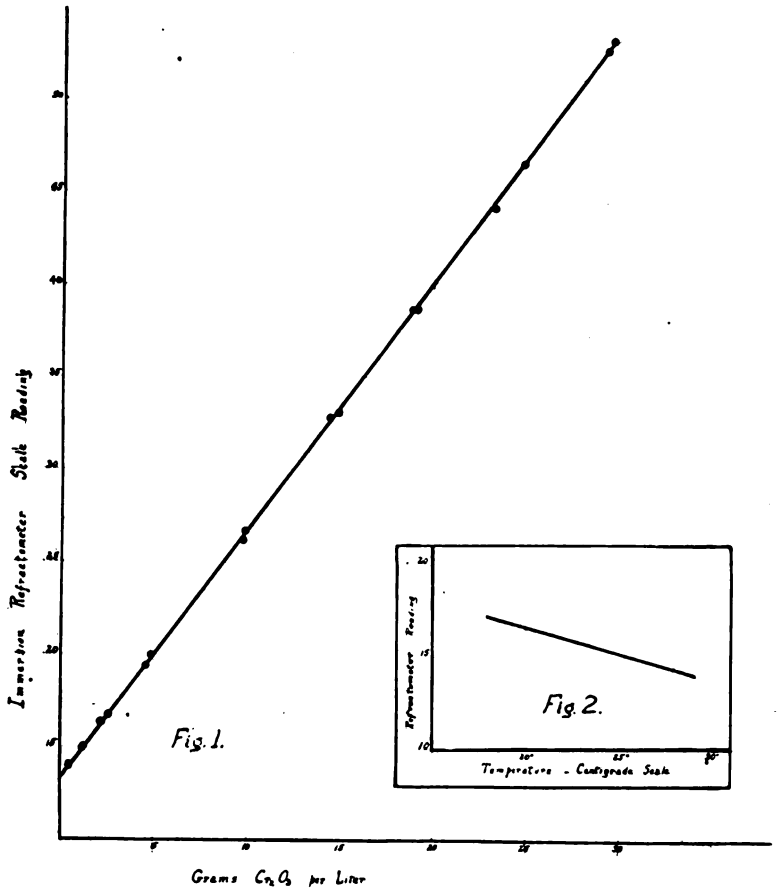
method has an accuracy of 0.1 gm. of Cr_2O_3 per liter, if a water bath maintained at a constant temperature of 25° C., is used.



We take pleasure in acknowledging the generous support of Messrs. A. F. Gallun and Sons Company in this investigation.

Columbia University,
New York City.

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WHAT DO WE REALLY DETERMINE AS VEGETABLE TANNING MATTER?

By E. Schell.

(Translated from *Le Cuir*, IX, 491-3 (1920).)

In reading the recent article by J. A. Wilson and E. J. Kern[1] on the determination of the true tanning value of vegetable tanning materials, doubt arises as to whether it is possible that the learned men of the entire world, after several decades of discussion and official interchange of ideas, really have been mistaken to the extent of giving us a method of analysis of vegetable tanning materials of such doubtful value as to be liable to an error of from 43 to 220 per cent. in the determination of the active constituent, as is indicated in Table II of the author's paper.

Their criticism applies directly to the shake method of the A. L. C. A., but as our European method is based upon the A. L. C. A. method and gives results differing by only a few tenths of one per cent., their criticism of the former method applies quite as much to ours and even more strongly to the old filter bell method.

Let us first of all say a few words regarding the origin of tannin analysis. Long before there was any question of analyzing the tanning materials used in the leather industry, medical science was using the astringent matter of oak galls and naturally required the production of the active principle in a more or less pure form. An analytic control of this medicament was created and its development was stubbornly pushed by the various scientists who occupied themselves with it. For a long time all tannin analyses were based upon this "tannin by ether" of the apothecary, since it was the purest commercial tannin and was considered 100 per cent. pure in the dry state.

But, through a study of the widely different tanning materials used in the industry, we came to appreciate that their constitutional differences are too great to permit their being based upon this single standard. Fortunately all tannins were found to possess certain properties in common and especially that of being absorbed by hide substance. The analogy of this absorption to the principal industrial application of the tannins caused prefer-

[1] *J. I. and E. C.*, 12, 465-9 (1920); This JOURNAL, 15, 295-308 (1920).

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ences to be given to methods of analysis based upon the absorption of tannin by hide substance, or hide powder. An attempt was first made[2] to determine tannin directly by noting the increase in weight of hide substance after absorption of the tanning material, but the faults of this procedure, which were quickly recognized, arose from the solubility of the hide substance and the partial reversibility of the absorption of tannin during the subsequent washing required to eliminate the absorbed non-tannins. We have thus been led to adopt the modern method of indirectly determining the tannin, which is taken as the difference in weight of the residues from a given solution of the material before and after detannization under strictly defined conditions.

It should be noted to the credit of our present method that it shows a purity of only about 90 per cent. for the purest commercial "tannin by ether," like the best "Schering" brand before the war.

The foregoing indicates precisely what we really determine.

In detannizing a solution under the conditions imposed by the official method of the Society of Leather Trades' Chemists,[3] we operate according to the best of our present knowledge and for the best interests of all parties concerned. This delicate separation of tannins from non-tannins has been the subject of official discussions of scientific specialists from all parts of the world. The actual analytic results give the value of all astringent principles utilized by the tanner. While we appreciate perfectly well that our method is not perfect, it has fewer faults than any other that has been recommended.

But utilizable tannin or matter absorbable by hide powder does not mean tannin capable of firm fixation by hide substance in so short a time as used in the method of Wilson and Kern. Who, indeed, would agree with them on the value of gambier, for example, which is already underestimated by the shake method because of the fixing of catechutannic acids to the detriment of the full value of the catechins, however valuable these may be.

All our modern theories of tanning agree in admitting a primary or immediate tannage and a secondary or later tannage. Al-

[2] Bell-Stephens, *Dingler's Journal*, 20, 168 (1826).

[3] *J. S. L. T. C.*, I, 103 (1917).

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though the real nature of vegetable tanning is still unknown, comparison may be made with quinone tannage, the reactions of which have been determined and demonstrated by L. Meunier and A. Seyewetz.[4] Of a given quantity of quinone, only a part is firmly fixed by the hide fibers, while the remainder is reduced to hydroquinone and must again be oxidized before it can combine with hide to form a stable compound. It is probable that only the quinone or keto forms of the tannins are capable of combining immediately with hide substance in such manner as to resist subsequent washing, while the reduced, or enol, forms (which either exist in the original material or result from chemical changes during tanning) are capable of being absorbed only and will not resist being washed out.

It is known that tannin molecules contain aromatic nuclei in which the hydroxy groups may occupy different positions. According to the relative positions of these groups, the molecule shows a greater or lesser tendency to oxidation. When one hydroxy group occupies an ortho or para position with respect to the other, there is a tendency to form quinone-like peroxides.

However, in vegetable tannins we have to do, not with a single substance, but with complex bodies of various forms. Furthermore, these bodies undergo transformations from the time of their original formation in the plant until they are used. Consider also the complexity of the tannins of oak; those of the scurf, which we imagine as the migratory forms of the tannins of the leaves, are composed of at least two forms, so-called gallotannic acid and the leucotannin of Nierenstein; and these are different from the tannins of the wood and bark.

According to Powarnine[5] also, only a part of the tannin mixture can be fixed by the hide immediately, while the other part is absorbed in the enol form and may be washed out immediately after tanning, although it slowly changes into the keto form, whereupon it becomes firmly fixed.

It therefore does not seem fair to base the true tanning value only upon the portion capable of immediate fixation, when this represents only a fraction of the total utilizable tannin.

[4] See abstract This JOURNAL, 3, 245 (1908), and Meunier, *Chimie et Industrie*, I, 71 (1918); This JOURNAL, 13, 530 (1918).

[5] *Collegium*, 1912, p. 105; This JOURNAL, 7, 337 (1912).

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It seems to us that the Wilson-Kern method cannot pretend to determine the total practical value of a tanning material, but only that portion which is capable of fixation by hide in a relatively short time. Furthermore, this portion depends not only upon the tannins present, but also upon the nature of the raw material.

[*Translator's Comment:* Schell's defense of the official methods is not convincing, since he offers no facts upon which a defense could be based. The result obtained for "tannin by ether" proves nothing inasmuch as it is evident that the official methods should give more nearly correct results the purer the sample. Thus far, defenders of the official methods seem to have carefully avoided discussion of the curves presented by Wilson and Kern which show how widely the per cent. tannin found by the A. L. C. A. method varies with changes in proportion of hide powder used, whereas no one has yet explained why the results obtained using 12.5 grams dry powder per 200 cc. tan liquor should be accepted as correct. Schell's argument based upon the assumption of the existence of two kinds of tannin, corresponding to quinone and hydroquinone, is destroyed by his analogy, since hydroquinone apparently has no tanning properties and should therefore be classed as a non-tannin. It would be no more logical to class hydroquinone as a tanning agent than to class carbon as a violent poison because of the properties of one of its oxidation products. The fact that there are certain non-tannins which, by oxidation or otherwise, are convertible into tanning agents has been recognized by Wilson and Kern and dealt with in a paper entitled "Nature of the Hide-Tannin Compound and Its Bearing upon Tannin Analysis," which was presented at the 60th meeting of the American Chemical Society in Chicago, Sept. 8, 1920, and which has been accepted for publication in the December, 1920, number of the *Journal of Industrial and Engineering Chemistry.*—JOHN ARTHUR WILSON.]

ABSTRACTS.

Neutralization of Sulphonated Oils with Ammonia, Soda and Potash. By C. G. BUMCKE, *S. and L. Rep.*, Sept. 30, 1920, 69. Sulphonated oils previous to neutralization contain—(1) sulpho-fatty acids, (2) oxy-fatty acids, (3) fatty acids, (4) unchanged glycerides, and (5) sulphuric acid. Upon neutralization the small quantity of free sulphuric acid is neutralized first, then the sulpho-fatty acids and finally the fatty acids. Only a small quantity of the fatty acids are neutralized when the oil becomes clear. The process of neutralization is the same whether soda, ammonia or potash be used, although potash is seldom used now on account of price. The ammonia soaps make the oil more limpid and keep it liquid at lower temperatures than soda soap. Most oils are neutralized with soda and ammonia, the soda representing from 70 to 90 per cent. of the alkali used in neutralizing. In discussing the acidity of sulphonated oils, attention is

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called to the error in applying the usual acid value titration to sulphonated oils containing ammonia.

Modern Methods of Liming. *Lea. World,* 1920, 30 *et seq.* An article dealing with the various methods of liming. The advantages of the recently introduced Forsare and Tilston-Melbourne processes are discussed.

Estimation of Sulphide. Committee on Limeyard Control, III. By J. E. PICKLES, *J. S. L. T. C.*, 4, 231 (1920). For the estimation of sulphide in samples of sodium sulphide the following method is proposed: About 70 cc. of cadmium acetate solution (62 grams cadmium acetate in 250 cc. glacial acetic acid and 2,250 cc. water) are placed in a 300 cc. conical flask and the solution to be tested added. After thoroughly mixing the contents by shaking, the precipitate of cadmium sulphide is filtered off and washed twice with distilled water. The precipitate is washed back into the flask, 2 cc. glacial acetic acid and 50 cc. (or excess) N/20 iodine added and allowed to stand for about 2 minutes. The excess iodine is then titrated with N/20 thiosulphate solution using starch solution as indicator. For the determination of sulphide in lime liquors the apparatus used in steel analysis for the determination of sulphur, is made use of, CO_2 being used instead of H. Cadmium acetate is added to the receiving flask and the air is removed from the apparatus by passing CO_2 through rapidly. The solution to be tested is added to the distilling flask, followed by 5 to 10 cc. concentrated HCl. The solution in the distilling flask is brought to the boil and continued until the solution in the receiving flask boils when the burner is removed and CO_2 passed through the apparatus for 5-10 minutes. The precipitate of cadmium sulphide in the receiving flask is filtered off, washed, returned to the flask and treated as above. 1 cc. N/20 iodine = 0.00195175 gram Na_2S or 0.00085 gram H_2S. It was found by experiment that a practical maximum for the distillation method was reached when about 40 milligrams H_2S distilled over, beyond this amount the precipitate becomes unwieldy.

Effect of Neutral Salts on the Basicity of Chrome Liquors. By B. B. DHAVALE and S. R. DAS, *J. S. L. T. C.*, 4, 225 (1920). Results of experiments are given to show that the addition of sodium chloride to a basic chromium sulphate solution increases the acidity of such solutions as determined by the Procter and McCandlish method. By the gradual addition of sodium chloride the basicity of the solution was found to increase to a maximum which appeared to be reached when the proportion of Cr to NaCl was as 1 : 281.

The authors also found that the acidity result was appreciably influenced by: (1) the temperature at which the titration was made and (2) the rate at which the alkali was added.

Chrome Tanning, I. By D. BURTON, *J. S. L. T. C.*, 4, 205 (1920). It is shown that violet chrome solutions tan more rapidly than green solutions of the same basicity figure, chrome and neutral salt content. An

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explanation is offered based on the higher acid (hydrion) concentration of the green solution which leads to the conclusion that the properties of chrome leather are influenced not only by the percentage of chrome but also by the degree of basicity—or extent of neutralization—of the chrome salt on the fiber.

The completion of tannage is shown to be best judged from the feel (absence of horniness and curling at the edges) of a piece of the leather after boiling, which must be neutralized before boiling, despite the fact that there will be a distinct shrinkage if this condition be obtained. This indicates that it may be possible to accelerate tanning in practice, as it is unnecessary to leave the pelt in the liquor in the one bath process till it stands the boiling test, and if feel be accepted as the criterion, tannage need not be carried so far. This also applies to the two bath process where the leather is nearly always acid when it leaves the second bath.

The factors which determine the tanning properties of a chrome liquor are: (1) the strength or percentage of chrome, (2) the acidity or acid (hydrion) concentration and not the basicity as now determined, *i. e.*, the ratio, $\frac{52 \times \%\text{ Total acid in boiling solution,}}{\%\text{ Cr.}}$ just as in vegetable tanning the properties of a liquor cannot be defined by the strength and acidity without taking into account the astringency. The basicity figure is no criterion of the hydrion concentration and is shown to be inadequate since liquors of the same chrome percentage basicity figure and even neutral salt content have widely different velocities of tanning. It also fails to take into account acids like carbonic acid and sulphurous acid (liable to be present in excess in SO_2 chrome liquors) which affect the properties of a liquor.

Magnesium Sulphate in Vegetable Tanned Leathers and Its Effect upon Analytic Results. By E. JALADE, *Le Cuir,* IX, 467-71 and 484-86 (1920). The presence of Epsom salt in leather to the extent of less than 1 per cent. is permissible for several reasons. It is the addition of this salt to the tan liquors that makes modern rapid tannages possible; it clarifies the liquors, eliminates the difficulties of drying, and gives the grain a better color. But the introduction of larger quantities into leather for the purpose of weighting is fraudulent.

Special precautions are required in the analysis of leathers containing much magnesium sulphate. The ordinary moisture determination will always be too low because the magnesium sulphate retains a portion of its water of crystallization. The determination of ash, too, will be low because the ignition in the presence of organic matter causes a reduction and loss of a considerable proportion of the sulphate. In order to avoid these errors, it is necessary to determine the total quantity of MgO present and calculate it to $MgSO_4.7H_2O$. J. A. W.

Use of Sodium Sulphite and Sodium Bisulphite in the Tannery. By B. KOHNSTEIN, *Coll.,* 597, 46, 1920, from *Häute und Lederberichte,* 38, 5,

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1919. These sulphites are used not only by the extract manufacturers for sulphited extracts, but also by the tanners in dissolving difficultly soluble solid and liquid extracts. Their use not only reduces insolubles but also produces a bright color and prevents fermentation on standing and storage. For sulphiting solid quebracho extract, 5,000 kg. of extract are treated with hot water until practically dissolved and then are boiled with 120 kg. sodium sulphite, 150 kg. sodium bisulphite and 25 kg. aluminum sulphate. After boiling, 10 liters of acetic and 5 liters of formic acid are added. The aluminum salt gives the quebracho a bright red color while the acids free a part of the sulphurous acid which not only bleaches but also prevents fermentation; formic acid too has a disinfecting action. Strongly sulphited extracts are quickly absorbed by the hide, but also are easily washed out and give little weight. Leather from such extracts is short fibered and brittle, especially so after storage. During the war pine and oak were often leached with addition of sodium sulphite, but generally too much sulphite (up to 15 per cent. of weight of tannin) was used and of course poor leather resulted from it. Sulphite is still used to aid in leaching, but is never added to the fresh tanning material. A mixture of Na_2SO_3 and $NaHSO_3$, equal to 3 per cent. of the weight of the tanning material, is dissolved in the water which goes onto the nearly spent material and is gradually worked back to the fresh. A 1 to 1½ per cent. solution of $NaHSO_3$ can be used in a drum or paddle for deliming skins, after the bisulphite the skins are treated with weak HCl or lactic acid and rinsed with water. Na_2SO_3 in place of thiosulphate has been used in 2-bath chrome tanning, but great care must be exercised in the reduction because of excessive heating which may take place especially in rapidly rotating drums. Na_2SO_3 has an advantage, however, in that the troublesome separation of sulphur does not occur. I. D. C.

Contribution to the Study of Unhaired Skins (Determination of Lime in Unhaired Skins). By G. GRASSER, *Coll.*, 598, 80, 1920. The usual determination of CaO in unhaired skins by ashing, while sufficiently accurate for tannery control, is subject to some error because small amounts of other metals (K, Na, Mg, Si) are included and is also troublesome because the fused slow-burning carbonaceous lumps often require at least 2 hours blasting to secure a white ash, even when moistened with NH_4NO_3 or HNO_3. These difficulties are avoided by wet oxidation with HNO_3. The unhaired skin, after removal of excess of water by gentle pressure between woolen cloths, is cut into very thin strips from which 5 grams are weighed into a 800 cc. beaker, 50 cc. water and 3 cc. concentrated HNO_3 are added and the solution boiled gently. After about 10 minutes a bright yellow slightly cloudy liquid is obtained. The cloudiness is due to keratin fibers from which, however, all CaO has been dissolved. The solution is cooled, neutralized with NH_4OH, acidified slightly with acetic acid, diluted to 150 cc. and filtered. CaO is precipitated in boiling solution with 20 cc. saturated $(NH_4)_2C_2O_4$, the precipitate is filtered, washed with dilute $(NH_4)_2C_2O_4$, ignited, and weighed as CaO as usual. I. D. C.

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Leather Greases in the Years 1914-1918. By SMAIC and WLADIKA, *Coll.*, 597, 29-38; 598, 81-90 (1920). During the war there was a great dearth of leather greases due to the fact that foreign raw products could not be obtained. The demand could be met only by mixing the usual animal fats with cheaper products or by using substitutes. Paraffine and mineral oils were the materials usually mixed with the animal fats, while the substitutes commonly consisted of paraffine or mineral oils mixed with soap in such proportions that the resulting product would readily emulsify in water. The animal fats were required by law to be mixed with cheaper and more plentiful greases, and the amounts prescribed for some of these products were as follows: fish oil with 30 per cent. mineral oil; degras with 30 to 50 per cent. mineral oil; tallow either with 30 per cent. paraffine or with 32 per cent. bone grease and 30 per cent. paraffine; stearin with 30 per cent. paraffine. Numerous tables are given showing first for comparison the analysis either of the pure or of the pre-war materials and then the analysis of the various mixed greases and substitutes in use during the war. Quite often much more than the allowed amount of mineral oil was found present in the mixed greases. The fatty acids from tallow, remaining after the glycerine had been removed for the manufacture of munitions, could not be used as such for free oleic acid spues and also produces a brittle leather. But by partially neutralizing the mixture of acids, either with sodium or preferably with ammonia, a very good grease was obtained. Soaps also were adulterated, one sample, a "wash soap," containing 68 per cent. kaolin and only 5.8 per cent. soda soap. Leather preservatives, consisting of paraffine and mineral oil in varying proportions, were used in large quantities during the war, especially by the army, but they have now largely gone out of use. I. D. C.

Oil (Chamois) Tannage, III. By W. MOELLER, *Coll.*, 597, 12-17 (1920). Fahrion's objection (*Coll.*, 590, 165; 595, 365 (1919)) to Moeller's theory of oil tannage, in which the assumption is made that amino-acids act as peptisers, was that the presence of these acids had not only not been proven but was also very improbable. Moeller states that his previous work (*Coll.*, 1918, 34) has shown the presence of an amino-acid group in collagen from which free amino-acids could be formed as one of the decomposition products of skins. The following source of amino-acids was, however, considered more probable. Fish oil contains substances very similar to lactones or acid-anhydrides, and these substances readily combine with ammonia to form amino-acids. The ammonia required could be produced during tanning by a slight decomposition either of the skin or of the fish oil. By analysis an unhaired skin was found to contain 0.9 per cent. nitrogen which was set free as ammonia by treatment of the skin with KOH, while a fish oil contained 0.09 per cent. of such nitrogen. This nitrogen could be present in the oil or skin either in an ammonia group or in an amino-acid group. Since only a very small quantity of ammonia is required to form a rather large amount of amino-acid Moeller considers it probable that enough amino-acids are formed from this source to satisfy his theory. I. D. C.

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Theory of Leather Formation. By W. FAHRION, *Coll.*, 599, 125-128 (1920); see *Coll.*, 597, 12 (1920). Fahrion considers that Moeller's theory of oil tannage is without foundation until he has proven that "1. NH_3 is set free in oil and also in alcoholic tannages, 2. that this NH_3 does not escape into the air, 3. that lactones or anhydrides, which can form amino-acids with NH_3, are really formed from the anti oxidation products of the unsaturated fatty acids of fish oil." In Moeller's work on aldehyde tannage (*Coll.*, 1919, 270), he states that treatment with formaldehyde was found to have no effect on the acid absorbing properties of hide powder, and bases his criticism of Stiasny's work (*Coll.*, 1908, 131) on this point. In examining Moeller's results Fahrion finds that there was actually a decrease in acid absorption by formaldehyde treated leather in 8 of the 12 determinations. Fahrion also found, by experiment, that formaldehyde treated hide powder absorbed only 3.1 per cent. HCl while untreated hide powder absorbed 3.78 per cent. HCl. I. D. C.

Formol Titration of Hide Powder and Aldehyde Tannage. By O. GERNGROSS, *Coll.*, 597, 2-11, 1920. Schiff's reaction of formaldehyde on amino-acids, by means of which the acid group is set free, was first applied by Sorensen (*Biochemische Zeitschrift*, 7, 45, 1908) as a quantitative method for acidity in studying complex amino-acids by formol titration. Stiasny (*Coll.*, 1908, 132) applied the method in titrating hide powder by determining the decrease in the ability of formaldehyde treated hide powder to take up acid. He found in all cases an appreciable decrease and that hide powder behaved similar to any other albumin, from which he concluded that in aldehyde tannage a chemical reaction took place between the hide substance and formaldehyde. Moeller (*Coll.*, 1919, 270) using a slightly modified method found no effect by formaldehyde on the acid absorbing power of hide powder, and questioned Stiasny's results because he neither neutralized his formaldehyde or removed the excess of it before titration. The importance of the subject led Gerngross to carry on some experiments. Twenty gram portions of unchromed hide powder were allowed to stand with (*a*) 500 cc. distilled water, (*b*) 400 cc. distilled water and 100 cc. formalin solution neutralized with 7.3 cc. 0.2 Molar $Ba(OH)_2$, (*c*) 400 cc. distilled water and 100 cc. unneutralized formalin solution. After removal of most of the solution by suction, the hide powder was dried first at 35° C., then at room temperature, and 3.0187 gm. portions were shaken up with 60 cc. of CO_2 free water and 25 cc. of 0.058 N formic, acetic, and HCl respectively. Aliquots of the filtrates from these were titrated with 0.1 N $Ba(OH)_2$ and phenolphthalein, and in all cases the formaldehyde treated hide powders absorbed less acid, the percentage decreases being with HCl 15, with acetic 45, and with formic 34. This method differed slightly from Moeller's but when his method was followed exactly a 14 per cent. decrease in absorption of HCl was found. If, as Moeller proposes, the decrease in absorption is due to the presence of formic acid from the formaldehyde, then equimolar quantities of various acids should all show the same decrease. However, with 8 acids (HCl,

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H_2SO_4, dichloracetic, oxalic, chloracetic, formic, acetic and propionic) the decrease expressed in cc. of 0.1 N acid varied from 1.9 cc. to 4.2 cc. The results show, however, "that increasing H ion concentration represses the action between formaldehyde and hide powder" which should be the case if the hide powder reacts in the same way as a simple amino-acid. While the results do not prove the presence of a free amino group, they do show that "hide contains at least one basic reactive group with which it can react similar to any simple compound." If, as Moeller suggests, the decrease in absorption is due to the formation of an impermeable coating of polymerized formaldehyde around the fibers, this same effect should be shown with alkalies. However, formaldehyde treated hide powder absorbed slightly more NaOH than the untreated powder. R. W. F.

The Nature of Quebracho Tannin. By W. Moeller, *Coll.*, 599, 106-9, 1920. Moeller's theory on the nature and properties of plant tannin colloids (*Coll.*, 1915, 441-51) requires that all plant tannins contain tannins of both broad classes, *e. g.*, pyrogallol and catechol. Some observations on quebracho, a generally accepted pure catechol tannin, are given in support of his theory. Analyses of one kind of sap wood from quebracho gave an average of 6.4 per cent. tannin and 2.2 per cent. non-tannins or a ratio of about 3 to 1 which is very different from the usual ratio of about 10 to 1 for the heartwood. The reactions of the aqueous extract of the sap wood also showed that it is different and that the tannin resembles those of the pyrogallol class while the heartwood clearly belonged to the catechol group. Trunks of quebracho trees with peculiar heartwood structure have also been noticed. In such trees there were in the heartwood streaks, 4 to 5 cm. or more wide of bright wood having the appearance of sap wood. These streaks occur not only at the surface but also entirely within the heartwood and sometimes extend from the roots to the upper part of the tree. Analysis of such trunks gave 7.8 per cent. tannin and 1.7 per cent. non-tannins. The reactions of the aqueous extract varied considerably from those of the normal quebracho wood and pointed to the presence of pyrogallol tannin. It should be stated here that Perkin and Gunnet (*J. Chem. Soc.*, 69, 1903) in examining quebracho tannin found substances such as ellagic and gallic acids which are in general characteristic only of pyrogallol tannins. Moeller makes the suggestion that the growing quebracho tree consists chiefly of sapwood with a little of the rich tannin bearing heartwood and that the formation of the heartwood tannin proceeds with age and by the changing over of the sapwood tannin into catechol tannin of the heartwood through oxidation and condensation in the sap streams. In favor of this are the results of Kranse and Manicke (*Chem. Berichte*, 53, 190-201, 1920) on the changing of members of the pyrogallol class, namely gallic acid, into derivatives of anthraquinone. It is possible that the peculiar vein formations mentioned were caused by queer growth which prevented their transformation. R. W. F.

Zapon and Zellon Lacquers and Their Solvents. By Fr. Zimmer, *Kunststoffe*, 1918, 92, through *Collegium*, 1910, 267. Nitro-cellulose is

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the basis of Zapon. Solvents are amyl acetate, acetone, acetone chlorhydrin, ethyl ether, epi-chlorhydrin, dinitrobenzol, methyl alcohol, nitrobenzol, carbon bisulphide, carbon tetrachloride, cyclohexanone formate and acetate. The Zellon lacquers are made from acetyl cellulose; solvents are mixtures of spirits, hydrocarbons, acetone with exclusion of amyl acetate, acetylene tetrachloride, boiling point 149°. This last can also be used with other solvents, such as do not alone dissolve cellulose acetate; alcohol and methyl alcohol additions, singly or united, serve well. Other solvents are ethyl acetate, benzoate, formate, etc.; symmetrical dichlorethylene, epichlorhydrin, mono- and di-chlorhydrin, nitrobenzol, trichlorethane, as well as other chlorinated hydrocarbons, also in mixture with spirit, acetone, wood spirit, etc. While the use of Zapon lacquer since several decades has been established as a firm foundation for metal, glass, etc., the recent Zellon lacquer has been employed specially for porous substances, textiles, leather, etc. W. J. K.

The Speed Rate of Deliming. By GEORG GRASSER, *Collegium*, 1919, 341-7. In practice reagents are used which give water soluble compounds with lime, such as hydrochloric, sulphuric, formic, acetic, lactic, butyric and boric acids, ammonium butyrate and chloride, sodium bisulphate, sodium bisulphite, cresol sulphonic acid and molasses. Some of these are in the market under protected trade names.

In some cases bateing and deliming are confused. For example, bran, a genuine bate, on ageing develops acid which delimes. The old practical rule is to use sour bran first and finish with sweet; if reversed, the sweet bate is, to be sure, effective, but the following acid bate again swells the hide. The artificial bates, Erodin, Sukkanin and Oropon have a similar action, but that of Purgatol is different; this contains the anhydrides of lactic and butyric acids, without fermenting power. Real acid is not present and when developed and immediately fixed by the lime produces no plumping and the lime salts formed make the hide fall.

The author measured the relative deliming velocities of the more important agents used by allowing 100 cc. of ½ per cent. solutions to act upon 14 gm. test pieces of plumped hide for heavy leather at 11-12° C. Sections were made at periodic intervals and the depth of penetration measured by use of phenolphthalein which reddened the layer still containing lime. It was found that sulphuric acid had completely delimed (100 per cent.) in ¾ hour; sulphuric acid + sodium chloride (equal parts), also sulphuric acid + sodium bisulphite in 1¼ hrs.; hydrochloric acid in 1¾ hrs.; ammonium chloride in 2¼ hrs.; hydrochloric acid + salt in 2¾ hrs.; sodium bisulphate, 3¼ hrs.; lactic or acetic acid, 5¾ hrs. After 8 hrs. the pieces were taken out of the remaining solutions for 40 hours interval after which the deliming with sodium bisulphite was complete; on replacing the others, Neradol ND was finished in 8 hrs. more, molasses in 56 hrs. more, while distilled H_2O still left a trace. Neradol ND is very weakly acid (10 gm. = 10 cc. N) hence the weak solution used here is insufficient for rapid deliming. For this reason tannage with these syn-

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thetic tans require lime free hide, since the active principle is free sulphonic acid.

Experiments were also made to study the influence of variation in process of liming upon the speed of deliming. Pieces of hide were treated in (1) straight limes, (2) limes sharpened with arsenic sulphide containing $Ca(SH)_2$, (3) limes sharpened with Na_2S containing $Ca(SH)_2$ and NaOH. The test pieces were then unhaired, rinsed and delimed in ½ per cent. solutions of (*a*) ammonium chloride, (*b*) lactic acid, (*c*) sulphuric acid + salt, (*d*) sodium bisulphate; sections were made at intervals and tested with phenolphthalein. It was found that the nature of the deliming agent had more influence than the liming method. Rapid deliming agents such as (*c*) and (*a*) had the common property of deliming the hide treated with straight lime or mixture (3) more rapidly than that from (2). On the contrary, the relatively slower deliming agent sodium bisulphate was slower with the hides from straight lime than from the others. The weak deliming organic acid (lactic) completely delimed the test from (2) in 3 hours, while (1) showed 69 per cent., (3) 67 per cent. A theoretical explanation of these differences is not evident, but it is suggested that rate of diffusion may be of influence. W. J. K.

Tanning Chemistry and Technique in 1919. By R. LAUFFMANN, *Ledertechn. Rund.*, 12, 65, 73, 84, 92, 102, 111, and 118. Of new books appearing in this year the following are referred to: (1) Untersuchungen über Depside und Gerbstoffe (Researches on Depsides and Tannins), by Emil Fisher, Verlag von Julius Springer, Berlin. (2) Die Edelkastanie, ihre volkswissenschaftliche Bedeutung, ihr Anbau und ihre Bewirtschaftung (The Chestnut, its National Scientific Importance, its Cultivation and Management) by E. Merz; to be obtained from the Secretary of the Swiss Inspection für Forstwesen, Jagd und Fischerie, Bern. (3) Die Fettstoffe des Gerbers (The Fatty Materials of the Tanner), by Dr. W. Fahrion, Vol. 3 from Bucherei des Gerber Verlag by Jos. Jeltmar. (4) Reprinting of the important work of F. Knapp on the nature and essence of tanning in the *Collegium*.

PREPARATION OF THE HIDE FOR TANNING.

B. Kohnstien (*Häute und Lederber.*, 1919, No. 44) treats of the nature of unhairing, the processes and materials used and the conditions to be considered in practise. Not only is the hair and epidermis to be loosened, but the natural fat of the hide is to be saponified in order to be removed in unhairing, since the latter makes the penetration of the hide by the tanning material and the coloring of the leather difficult and is a cause of stains. The manner and duration of liming as well as the use of "sharpeners" must be determined by the kind of leather to be produced. Lately, liming has been undertaken with pure sodium sulphide in drums or paddles.

In deliming, the strength of the acid and of the other materials used is of great importance. G. Grasser (*Collegium*, 1919, 341) has determined the deliming effect of hydrochloric acid, hydrochloric acid with salt, sulphuric acid with sodium bisulphite, sodium bisulphate, sodium bisulphite,

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acetic acid, lactic acid, ammonium chloride, melasse and Neradol ND by the action of ½ per cent. aqueous solutions of the materials on pieces of pelt and found the order of decreasing effect to be as follows: sulphuric acid, sulphuric acid and salt, sulphuric acid with sodium sulphate, hydrochloric acid, ammonium chloride, hydrochloric acid with salt, sodium bisulphate, lactic acid, acetic acid, sodium bisulphate, Neradol ND and melasse. The influence of the mode of liming, the use of pure limes and limes sharpened with sodium sulphide and arsenic sulphide, on the rapidity of deliming with ammonium chloride, lactic acid with salt and sodium bisulphate was investigated and it was found that the deliming effect was influenced less by the mode of liming than by the kind of deliming agent.

C. S. Fuchs (Ger. Pat. 313,995) produces an agent for deliming pelts from the liquors from the alkaline decomposition of vegetable materials. The liquors are freed of the constituents forming insoluble lime salts. Either the lignin acids are first precipitated with acid, filtered off, the filtrate neutralized or made weakly alkaline, evaporated to a suitable concentration and then weakly acidulated with acid, or the alkaline liquor is evaporated, cooled and treated with mineral acid, so as to leave a small amount of free acid present. In both cases the lignin acids are precipitated as a gelatinous precipitate which coagulate with moderate heat, are filtered off and supplied for specific purposes.

Shaving and splitting is usually undertaken on the lightly tanned leather and seldom on the green hides, since this work on untanned hide is made difficult by the hide adhering to the knife or roller. This evil is avoided by the process of C. Freudenberg (Ger. Pat. 308,506) where the hide or pelt after unhairing and during or after deliming is saturated with a concentrated solution of a non-tanning salt and then shaved or split in the usual manner. The split hide is freed from the salt by soaking in water and is then worked up in the usual manner.

With reference to the determination of the pelt weight, B. Kohnstein (*Häute und Lederber.*, 1919, No. 46) refers to the fact that the pelts can be made to swell or fall according to whether an old or new lime is used and according to the property and temperature of the lime liquors. Accordingly under different circumstances different quantities of water are taken up by the hide and a different pelt weight is obtained. The same hide will give a different pelt weight according to whether it is placed in cold or lukewarm water before draining. Therefore investigations concerning the determination of pelt weight should be carried out under the same conditions, especially with the same water, at the same temperature and with the same liming process.

Vegetable Tannins.

A. de Dominicis (through *Chem. Centralbl.*, 1920, I, 429) has carried out investigations on the biological importance of the tannins and found that the presence of vegetable acids (acetic, tartaric, citric acids) exert an arresting action on the coagulating effect of tannin on 1 per cent. egg albumen solution. From consideration of his investigations and of the

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data of earlier literature, the author arrives at the conclusion that the tannins are secondary products of metabolism.

W. Moeller in an earlier work (*Collegium,* 1915, 49) presented the view that the essential compounds contained in vegetable tanning material possessed a quinoid structure, and on that account there existed a close relation between quinone and vegetable tannage. Therefore the nature and properties of the different quinones, especially their stability in the presence of oxidation and polymerization agents, is of great importance to vegetable tanning. In a recent work (*Collegium,* 1919, 11) he treats of the structure and the polymerization and condensation phenomena of benzoquinone; its polymers and related bodies with special consideration of the chemical and physical relation to the vegetable tannins as well as the origin of phlobaphenes, their constitution and properties. For the formation of phlobaphenes, which according to Moeller also originate mainly in the plant substance, there are oxyanthraquinone, catechone and dihydroxyphenoquinon-dilactone as raw materials of quinoid character. The resulting highly colloidal complexes and phlobaphenes are changed to the peptized state by the addition of a uni- or polyvalent phenol.

K. Freudenberg (*Ber. D. Chem. Ges.,* 52, 1238) has carried out researches on chebulic acid. It contains a carboxyl group, is a fairly strong acid and displaces acetic acid in sodium acetate. On heating its aqueous solution to 100° it forms, in addition to gallic acid, another acid still unknown, and a substance with a carboxyl group, probably digalloylglucose, in which the unknown acid is united with sugar in the form of a glucoside.

J. Paessler (*Lederztg.,* 1918, No. 148, 153; 1919, No. 6, etc.) discusses in detail the vegetable tanning materials and their tannins with reference to the constitution, composition, physical and chemical properties, wherein the connection of the latter with the origin of leather defects is considered. The behavior of the different tannins and tanning materials toward the different agencies encountered in production, storage and use, especially toward moisture and heat, which are of great importanec with regard to a profitable utilization of the tannin in the tanning material.

In a further treatise (*Ledertechn. Rund.,* 1919, Nos. 13-24) Paessler produces data on the tannin content of oak wood, on the conditions which influence it; on the production of oak wood extracts; on the behavior of oak wood tannins on leaching the wood and the influence of temperature; on the properties and reactions of oakwood tannins; on the quality, examination for purity, price, tanning use and action of oakwood extracts; on the properties of leather produced with it as well as on the tanning and economic advantages resulting from the use of oakwood extract.

Again Paessler (*Ledertechn. Rund.,* 1919, Nos. 1-8) treats of the nature, handling and supplying, sale, production, and the composition of Knoppern; the properties and reactions of Knoppern tannins; the behavior of Knoppern on extraction and the properties of the liquor obtained; and the use of Knoppern. He furthermore describes some other galls, especially Rove (bassora gall nut) and finally gives a detailed bibliography on Knoppern and Galls.

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W. Eitner (*Häute und Lederber.*, 1919, No. 50) treats of the production of Austrian domestic tanning material. The tanning material most used there is pine bark; but still larch and alder bark as well as alder fruit approach it in importance, while pine twigs and cones are not suitable for tanning purposes. Eitner further remarks, that the tannin content of coniferous fruits like most other fruits depends on the maturity. Thus, for example, in the cones of the sea or beach fir there was found 8.2 per cent. in the green condition and in the fully ripened condition 3.2 per cent., in the cones of domestic Austrian pine 3.7 per cent. and 1.4 per cent. tannin was found. The fruit of the white alder in the unripe condition contains up to 17 per cent. tannin and of the black alder up to 12 per cent.

A Treatise by Schmidt (*Ledertechn. Rund.*, 1919, 41) contains data on the scaling of tan bark in storage, also a description with illustrations concerning the mechanical devices for conveying and disintegrating of bark and the arrangement of bark mills with reference to fire prevention.

According to a process by E. Reiss (Ger. Pat. 304,387) the stalks of the tannin containing hops are worked up into fibers suitable for spinning. The hop stalks after extraction with water are treated with solutions of caustic alkalies, sodium sulphide, sulphite, etc., for removal of pectin like materials. From liquor obtained a material can be recovered which can be used in tanning or dyeing.

B. Kohnstein (*Häute und Lederber.*, 1919, No. 45) indicates means to prevent injurious fermentation in and damage to tan liquors. Mineral materials that have proven suitable for this purpose are borax (to 1,000 liters of liquor 3½ kg. of borax), boric acid, sodium and ammonium fluoride; of organic materials, phenol, wood tar, condensation products of this with formaldehyde in weakly alkaline solution, salicylic acid and sodium salicylate are frequently used for this purpose. Kohnstein recommends addition of a small amount of naphthene sulphonic acid also of water soluble mineral oil and remarks that on the addition of materials of alkaline reaction air must be excluded as much as possible on account of the strong tendency of the tanning materials to oxidation. For this purpose some mineral oil is poured on the surface of the liquor. The formation of moulds and slime is likewise prevented the best by covering the liquor with oil, pumping off occasionally and filtering through tan bark. An addition of extract of mustard, mustard seeds or meal is unfavorable to the formation of slime. In another treatise (*Häute und Lederber.*, 1919, No. 28) on the use of sodium sulphite and sodium bisulphite in the tannery, Kohnstein describes the use of these materials in the leaching of tanning materials and in the sulphiting of tanning extracts. The use is largely with spent tanning materials and in such a way that 3 per cent. of a mixture of sodium sulphite and bisulphite on the weight of the materials is dissolved in the water required for leaching, the solution is pumped onto the nearly spent material and boiled or the solution is run onto the old tanning material and gradually pressed over to the fresh material. On sulphiting tanning materials, 5,000 kg. Argentine quebracho extract, for example, is

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dissolved as far as possible in hot water, then boiled with 120 kg. sodium sulphite, 150 kg. sodium bisulphite and 25 kg. aluminum sulphate and finally after boiling has been stopped 10 liters of acetic and 5 liters of formic acid are added. The aluminum salt contributes to the brightening of the color and the acid liberates a portion of the sulphurous acid which arrests fermentation.

G. Grasser (*Häute und Lederber.*, 1919, No. 45) treats of the Chemical Technology of Tanning Extract and describes the composition of the tanning material, the important conditions to be considered in leaching and the practical production of extracts.

The patented process of Töpfer and Müller described by Smaic and Wladica (*Häute und Lederber.*, 1919, No. 40) for evaporating and drying of tanning and other liquids consists essentially in spraying of the liquid to be dried in a very fine spray into a closed space by means of compressed air with simultaneous evacuation for the continuous removal of water vapor. Among the advantages of the new process, the authors stated that an unfavorable chemical or physical change of the liquor is prevented and that a powdered extract with only a little moisture is obtained. W. Moeller (*Gerber*, 1919, 189) confirms these statements, but does not consider the latter property an advantage since such extracts easily absorb water again on account of which it is difficult to obtain a true average sample on sampling.

According to the process of L. Bruml and R. Silberberger (Ger. Pat. 306,529) a very valuable tannin extract is obtained from pine bark by removing the resin with a suitable solvent, and after expelling the solvent, leaching in the usual way with water. As opposed to bark from which resin has not been removed, an increased yield of tannin is obtained.

M. Tejessy (*Häute und Lederber.*, 1919, No. 42) discussed the expediency of the establishment of a heating pump in extract factories and calculates that in the extraction of 30,000 kg. of pine bark about 30,000 kg. of fuel is obtained in the form of spent material. With the use of a triple effect, including the loss in conductance and in the power plant, about 80,000 kg. of steam are consumed of which but a half is consumed for evaporating the liquor. This means that a large quantity of fuel could be saved by the introduction of a heating pump which compresses the steam from the liquors to the necessary tension for heating purposes. In this manner the whole plant would consume only 50,000 kg. of steam instead of 80,000 and even 13,000 kg. of fuel could be spared also from the leather factory.

With reference to the qualitative testing of vegetable tanning materials, the following work appeared. R. Lauffmann has simplified his process for the determination of the molybdenum number (*Ledertechn. Rund.*, 1912, 353) which serves to indicate the tannins (l. c. 1919, 93; abst. this JOUR., 15, 435, 1920). Lauffmann (l. c. 1919, 61) has also investigated the behavior of tannin extract with the pine shaving reaction and the products obtained by potash fusion and indicates an exact method of procedure of

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potash fusion as well as a process based on the pine shaving reaction for testing and distinguishing the tannins.

G. Grasser (*Collegium*, 1919, 309) investigated the behavior of extracts of pine bark, chestnut wood, quebracho wood, mangrove bark, sumac, valonea, knoppern, gallnuts and gambier with the qualitative test for sugar with orthonitrophenylpropiolic acid. With gallnut, knoppern, gambier and quebracho extracts which contain very little sugar, he obtained a positive reaction (blue coloration) as also was the case with a sample of technical tannin. With another sample of quebracho extract no reaction was obtained. Grasser determined by further investigations that the defect in the reaction with quebracho and tannin is not brought about by the separation of sugar in the tannin molecule, but by sugar-like substances existing as such. With waste cellulose liquor, formaldehyde Neradol D and ND and Ordoval a negative reaction resulted. He concludes from his investigations, that from a positive result with the above reaction on tanning extract an intentional addition of sugar cannot be concluded without further confirmation; with leather, only a deep blue coloration can be claimed as a positive reaction.

Theory of Tanning.

The question, whether tanning is a purely chemical or physical (colloid-chemical) process is debated further by W. Fahrion (*Coll.*, 1919, 51, 165 and 356) on one side and by W. Moeller (*Coll.*, 1919, 61, 237, 270) on the other, especially with reference to chamois and aldehyde tanning. Fahrion retains his chemical conception of chamois and aldehyde tannage while Moeller endeavors to prove that for these tannages also the chemical theory of tanning has no authorization, whereas his peptization theory of tanning is applicable to them also. Moeller has also found that dégras (*Coll.*, 1919, 61) which in contrast to train oil is no longer capable of oxidation, and hydrocarbons (*Coll.*, 1919, 72) such as mineral oil and paraffine, tan, and yield products similar to chamois leather if the lacking pepitizators are added to the oil, for which phenol proves itself especially suitable. This fact Moeller also draws on as evidence of the correctness of his tanning theory.

In another treatise Moeller treats mineral tanning (*Coll.*, 1919, 101 and 347) also from the standpoint of the peptization theory, and especially attacks the conception of Abegg and von Schroeder who have concluded from researches on the action of formaldehyde on gelatine on the one hand and of aluminum, iron and chrome compounds on the other that tanning with formaldehyde is entirely different from tanning with mineral tanning materials. Moeller remarks that solutions of the sulphate of iron, aluminum and chrome of themselves are only weak tanning materials and will be only transformed into a peptized system by the hide, that the conditions sufficient for complete tannage, however, will only be created by special additions. Aluminum sulphate, for example, is changed into the peptized state only with difficulty when alone, but easily on the addition of salt; because of the increased dissociation, owing to the latter, splitting of the

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aluminum sulphate is favored and thereby a colloidal peptized solution of aluminum hydroxide is formed in non-peptized aluminum sulphate.

Vegetable Tanning.

J. Paessler (*Lederztg.*, 1919, No. 75 et seq.) treats of some points of importance for the leather industry; among others, the conditions which influence the leather yield in the different bark tannages. The observation of Courtier, that the content of hide substance and water is the same for all pelts and that the tannin in the several kinds of bark tanned leather differs, is disproved through the results of the work of von Schroeder and Paessler on the composition of hide and leather. The connection between the composition and yield of leather is discussed; the appropriate use of tanning material and the expedient execution of the tannage is described.

Chrome Tanning.

With reference to the use of sodium sulphite as a substitute for thiosulphate for reduction in the two-bath process, B. Kohnstein (*Häute und Lederber.*, 1919, No. 38) states that with its use, especially in quickly revolving drums, considerable rise in temperature occurs on account of which the hides are easily damaged, on the other hand the advantage exists of the non occurrence of the irksome precipitate of sulphur.

K. Schorlemmer (*Ledertechn. Rund.*, 1918, 61) had described a method for converting chrome into chromate by use of hydrogen peroxide as oxidizing agent and in a further work (*Coll.*, 1919, 5) found that complete oxidation with hydrogen peroxide in the presence of organic matter is not attained, but an addition of $FeCl_3$ promotes it and counteracts the arresting action of the organic matter. In the presence of considerable quantities of organic matter, oxidation with hydrogen peroxide cannot be carried out completely. Schorlemmer found further that by oxidizing the chrome with potassium permanganate the organic matter present is completely destroyed and correct results can be obtained. Nevertheless, oxidation with hydrogen peroxide on account of its simplicity is to be preferred wherever feasible. The organic matter of a chrome liquor, however, could be destroyed by evaporation of the liquor and ignition of the residue.

Other Mineral Tanning Processes.

W. Eitner (*Häute und Lederber.*, 1919, No. 36) treats of iron tanning and the products obtained, partly according to the work of Knapp and partly from individual researches and experiences. According to Eitner, in iron tanning, also, liquors of weaker strength must be used first followed by liquors of increasing strength. In this matter a serviceable bottom leather, and in combination with chrome, an especially elastic product is obtained. Iron tannage is not suitable for upper leather on account of its hardening and stiffening action. A combination of chrome tannage with subsequent iron tannage, however, produces good fine leathers.

G. Grasser (*Gerber*, 1919, 262) states that iron tannage has become of more importance in the face of the present increasing prices of chrome tanning materials; the patented process of iron tanning of Knapp, Rohm and Bystron-Vietinghoff are described and he concludes with some obser-

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vations on the finishing and dyeing of iron tanned leather. R. Lauffmann (*Zeitschr. f. öff. Chem.*, 1919, 27) also gives a compilation of patented processes for the production of iron leather.

Two patents by K. W. Mensing concerning the production of iron leather that is tough and durable on storing are given. The important points of one (Ger. Pat. 314,487) are that the tanning is carried out with ferric salt in the presence of an excess of oxidizing agent, and that the temperature of the iron solution used does not go materially beyond 35° whereby tanning can be effected from the beginning with strong ferric salt solutions. In another method of carrying out this process, the completely delimed pelt is previously treated with salts of weak alkaline reaction or basic aluminum or chromic salts and then retanned with neutral or weakly acid salts. Through the presence of an excess of oxidizing agent the dangerous presence of ferrous salts in the tan liquor and their formation in the leather is prevented; through observance of the prescribed limit of temperature the hydrolytic decomposition of the iron solution is prevented. The other process (Ger. Pat. 314,885) essentially concerns other after treatments of leather tanned according to the above; wherein the uncombined salts are washed out and the leather is treated with alkaline solutions after drying, or the iron tanned leather is treated with vegetable tanning material or with reducing agents. If leather tanned with ferric salt is treated with reducing agent, following a preliminary treatment with dilute acid solutions if necessary, then the ferric salt in the outer layer is reduced to ferrous salt and a partial removal of the tanning salt in the outer layer, a brightening of the leather and a mellower grain are produced.

A. Gawalowsky (*Häute und Lederber.*, 1919, No. 47) quotes a number of alums containing iron, zinc and copper which have not been used for tanning as yet and believes that many of these, for example, aluminum zinc alum as well as certain aluminates, for example, potassium aluminate, have a tanning action.

Other Tanning Materials and Processes.

An anonymous author (*Technik und Industrie*, 1919, 112) presents a brief communication on the use of formaldehyde in tanning and the products obtained thereby. G. Grasser (*Häute und Lederber.*, 1919, No. 43) describes the different groups of synthetic tanning materials and their importance for tanning. W. Buckow (*Coll.*, 1919, 211) investigated the composition and tanning properties of the new artificial tanning material "Corinal" and found that by its use, in combination with vegetable materials, tanning is accelerated and a leather is obtained having good properties.

Ger. Pat. 305,855 of the Badischen Anilin und Soda Fabrik concerns a method of carrying out the process according to Ger. Pat. 281,484, in which the hide is treated with water soluble hydroxylated aromatic compounds.

A. Gawalowsky (*Häute und Lederber.*, 1919, No. 41) in a treatise on the different processes of tanning, also mentions tanning with "Aseptolen,"

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that is, sulpho-phenolates and thinks that especially the iron, copper and zinc aseptolates are very well suited for tanning, since they preserve because of the sulpho-phenol and effect tannage through the metallic compound that they contain. He recommends especially iron aseptolate, designated chemically as ferrous sulphophenol-cresylate, upon the use of which for iron tanning W. Eitner (*Häute und Lederber.*, 1919) has also reported.

For the detection of artificial tanning material which contains phenols or phenol groups or sulphonic acids of phenols, R. Lauffmann (*Ledertechn. Rund.*, 1919, 89) gives a method which may be used for tanning liquids as well as leather. It consists of subjecting the dried residue of tanning liquids, or of the solution obtained by extracting finely divided leather with a 2 per cent. alkali solution, under observation to the conditions specified in the original of the potash fusion method, whereby phenol is reformed from the sulpho-acids. The phenol is shaken out of the solution with ether after the solution has been neutralized with sulphuric acid and finally made alkaline again with some ammonia. The ether is distilled off and in an alcoholic solution of the residue that has been treated with some ammonia, phenol is detected with the indophenol reaction. (Blue coloration in the presence of phenol after the addition of several drops of a solution of paraphenylenediamine-hydrochloride and of a solution of potassium ferricyanide.)

A number of treatises and innovations concerning sulphite cellulose lye, its preparation and value for tanning purposes appeared. A process by J. S. Robeson (Ger. Pat. 313,150) concerns the production of a tanning liquid from sulphite cellulose lye containing free ligno-sulphonic acid together with its salts. The concentrated lye liquor is treated with sulphurous acid and alkali sulphite or bisulphite so that all of the lime is converted into sulphate without leaving free mineral acid in the liquid. The lime and other bases, especially iron, remaining in solution as sulphate are precipitated by a considerable excess of oxalic acid.

C. Graf obtained a patent (Ger. Pat. 317,462) on a process for producing a substitute for tanning material by extracting vegetable tar with water. The solution obtained in this matter is added to waste sulphite liquor, together with glaubers salts, epsom salts or common salt if necessary. By the use of this tanning material a quick tannage is obtained and a leather of full tannage, light color and bright brown cut is produced.

Materials and Processes for Finishing of Leather.

A. Wagner (*Ledertechn. Rund.*, 1919, 101) discusses the different processes and appliances used until now for the moistening of leather, which however have the disadvantage that they either do not wet the leather through evenly or are too bothersome for large scale operations, and suggests to use for this purpose a process usual to the textile industries wherein the goods in a moistening plant are exposed to the action of a current of moist air.

B. Kohnstein (*Häute und Lederber.*, 1919, No. 40, 5) treats of the art, mode of use and action of oils, fats and fatty mixtures used in the leather

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industry for stuffing, and further relates that he has obtained good results on practical stuffing tests with methyethyl- and amyl esters of fatty acids. Spueing is prevented and the quality of the leather is improved by the use of these esters. He claims success in utilizing corn oil fatty acids for oiling leather which were not used for this purpose on account of their great liability to oxidation.

In a protected process by O. Röhm (Ger. Pat. 313,803) for the production of fat emulsions for oiling and oil tanning, the oil or fat to be used is emulsified by triturating with highly colloidal clay or similar mineral matter, if necessary with addition of a fluid solvent. In this manner fat is obtained which mixes more uniformly with water without separation and penetrates the leather easier, especially when oiling is accomplished with heat. Besides fat a fluid fat solvent like acetone or benzine can be mixed with it.

In order to make leather capable of resisting the action of chlorine, according to a process of P. Askenasy (Ger. Pat. 299,075), chlorinated oils, waxes or other mixtures produced according to Ger. Pat. 256,856 are incorporated with it which contain less than 30 per cent. chlorine.

A process by W. Rechberg (Ger. Pat. 317,418) for the production of a water-proof leather capable of resisting wear consists of saturating vegetable tanned leather with solutions of water-insoluble impregnating agents with addition of pyridine bases.

E. O. Rasser (*Bayr. Industrie und Gerberbeblatt*, 135, 41) discusses the recent progress in the domain of leather colors fast to light and water.

Leather.

R. Lauffmann (*Zeitschr. f. öff. Chemie*, 1919, 180) discusses the investigation of leathers of bark, mineral, chamois and artificial tannages; utilization of the results for judging of the kind of tannage and gives data on the composition of the different kinds of leather.

Tannery Wastes and Sewage.

A serviceable substitute for sole leather can be obtained according to a process by H. Mielenz and J. Schlossmann (Ger. Pat. 313,133) from the tendon-like wastes from slaughtered animals. Such waste parts are usually round, they are opened out by rolling, pressed into sheets and finally tanned.

J. B. Pérégrin (*Rev. des prod. chim.*, 22, 313) briefly refers to the applicability of waste chrome liquors of chrome tanneries for certain chemical processes, for example, oxidation of anthracene, phenanthrene, alcohol and glycerine.

A process for utilizing chrome leather wastes by A. Wolff (Ger. Pat. 310,309) consists in dissolving the waste in just a sufficient quantity of 5 per cent. sulphuric acid at 80-90° C. The separated fat is recovered by filtration or by skimming, then the chrome is precipitated at boiling temperature with an excess of milk of lime as chromic hydrate and worked up into chrome alum. The gelatine solution is freed from calcium sulphate and excess of lime and evaporated in a vacuum and thus a leather gelatine of light gray color is obtained.

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Various processes appeared concerning the use of leather scrap for the production of sole leather, for example, Ger. Pats. 306,052 and 306,702. Ger. Pat. 317,113 by E. Schöttle concerns the production of belting from leather scrap.

Miscellaneous.

P. Martell treats of the history of the descent of the domestic sheep (*Coll.*, 1919, 1) and of the domestic swine (*Coll.*, 1919, 206).

H. Kühl (*Ledertechn. Rund.*, 11, 53) discusses the procurance of suitable water for the tannery and, in this connection, the important process of softening water. According to the investigations of Kolb the permutit process of I. D. Riedel effects complete softening under specific conditions; still according to the researches of others, softening with lime or soda is to be preferred, and these latter processes are cheaper than the permutit. The softening process with the organic agent "Kana," which has been placed on the market by de Haen, Chemische Fabrik "List" is similar in its action to that with lime and soda and according to Kühl it is also possible to effect a practically complete softening with it. In contrast to the lime and soda process the application of "Kana" is said to possess the advantage of being easier and more simple. G. W. S.

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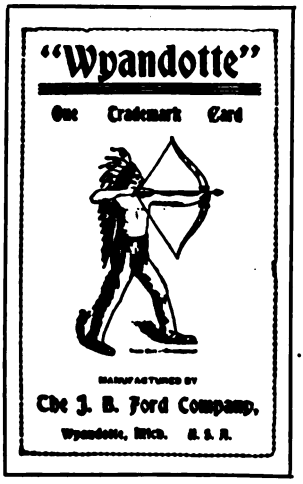

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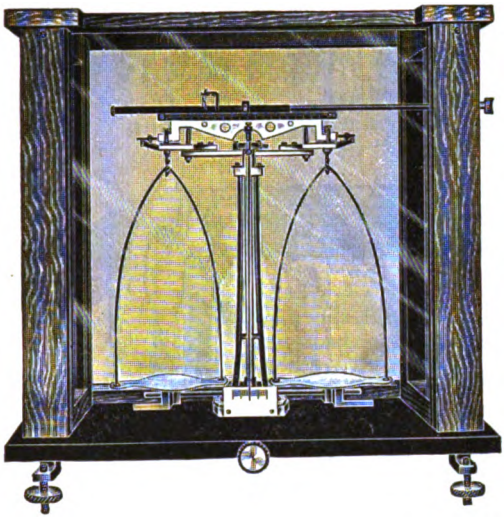

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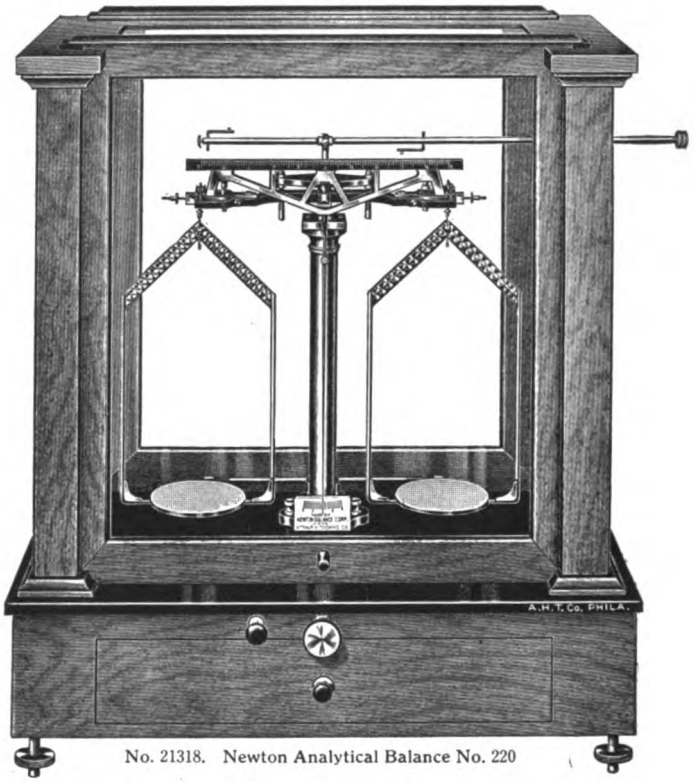

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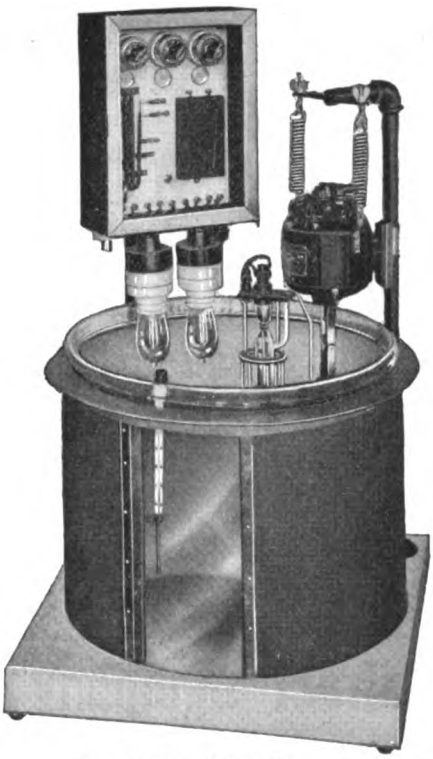

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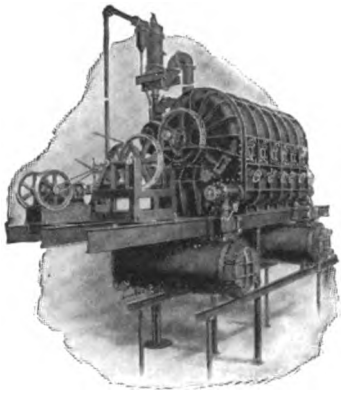

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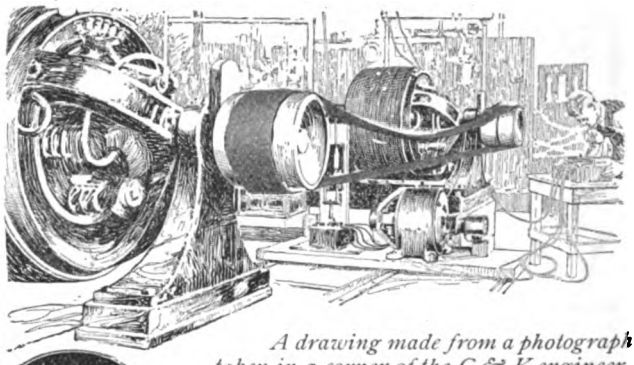

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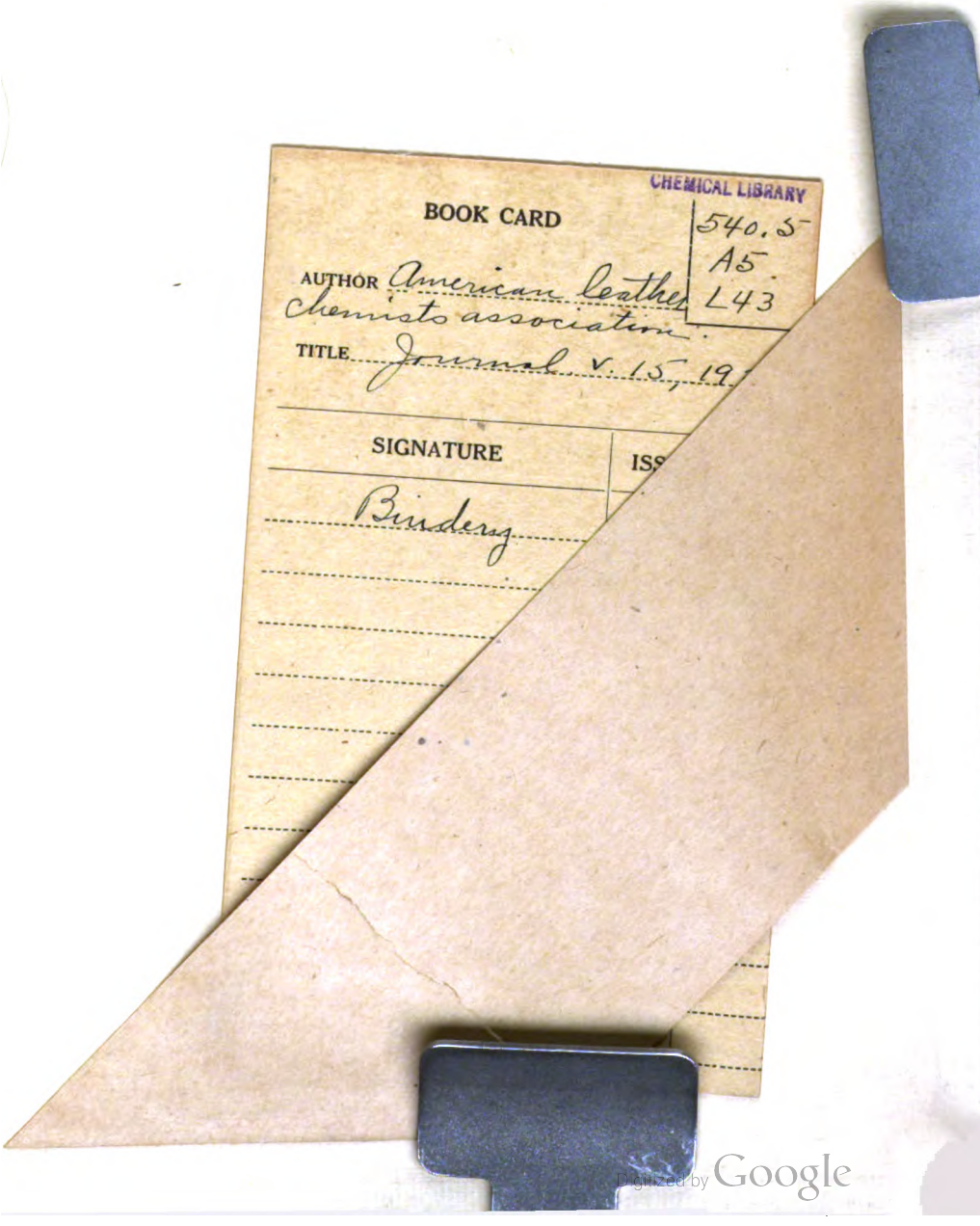

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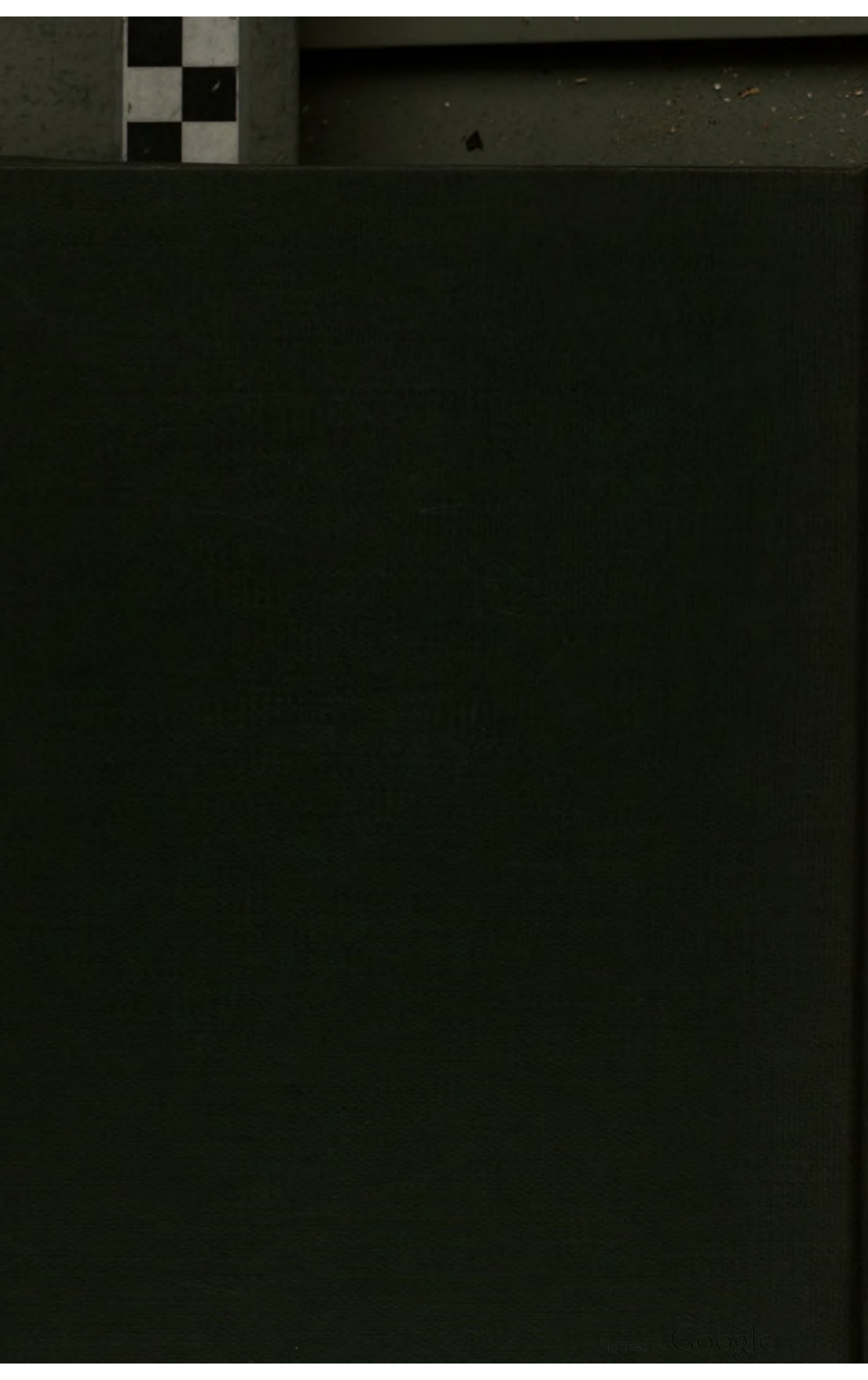
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